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THE SYNTHESIS OF POTENTIALLY CATALYTIC BIMETALLIC
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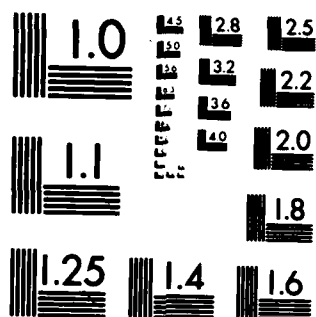
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A TRIDENT NUCLEAR PROJECT REPORT

NO. 15

THE SYSTEMS OF POTENTIALLY
CATASTROPHIC SIGNALING SYSTEMS



UNITED STATES NAVAL ACADEMY
ANNAPOLIS, MARYLAND

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Bimetallic Systems"

A Trident Scholar Project Report

by

Midshipman First Class Michael J. Golightly, 1982

U.S. Naval Academy

Annapolis, Maryland

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Abstract

Work this year has focused on the development of a synthetic sequence to the double metal system shown in Figure XIV (p. 19) which incorporates ferrocene as the backbone of the molecule. Such systems have the potential for hydrogen evolution from acidic solutions.

A route to the synthesis of 1'-benzylferrocenecarbinol (XIII), p. 22) involving the diketone intermediate 1-benzoyl-1'-o-chlorobenzoyl-ferrocene (XXIII) is discussed. XIII is used to synthesize the novel double metal compounds 1'-benzylferrocenecarbinol chromium tricarbonyl (XXIX, M=Cr) and 1-methylenediphenylphosphite-1'-benzylferrocene chromium tricarbonyl (XXX, M=Cr). An analogous compound, benzylferrocene chromium (XXX, M=Cr) triphenylphosphine dicarbonyl (XXXIII) was also prepared.

Background

Within the past 20 years, our society has come to realize that the traditional sources of energy such as coal, oil and natural gas are finite in quantity. This has forced a search for alternate sources of energy to meet the world's ever growing demands.

Complicating the problems of fossil fuel scarcity are the political instabilities which plague the oil rich countries of the world. In order to guarantee a long range, invulnerable source of energy, our country must look for indigenous, renewable sources of energy.

Three technologies which have been examined as future energy sources are nuclear power, synthetic fuels, and solar power.

Nuclear power, for all its technical sophistication, is not without problems. Although nuclear plants do not generate pollutants in the usual sense, they have their own unique problems. Reactor cooling in a power plant is accomplished by passing large quantities of water through the steam condensers of the plant. This coolant water is then returned to its source, several degree warmer than it started. Since the thermal losses from a nuclear power plant are high, the power plant causes the average temperature in the cooling water source to rise. This thermal pollution endangers the local ecosystem with wide economic impact on persons dependent upon the affected rivers and bays.

The problem of nuclear waste is only now being seriously addressed by Congress. While most persons are aware of the problems of spent nuclear fuel, few recognize that all plant materials exposed to the neutron flux of the core are activated to some extent and pose long term radiation hazards. It appears that the high cost and public concern about nuclear power makes it a questionable long term energy source.

Synthetic fuels or "synfuels" are the general name given to liquid fuels which are made by nontraditional sources. These include alcohol from fermentation and destructive distillation of wood, hydrocarbons from coal and tar sands and methane from animal wastes. These fuels are compatible with our present technology, but are generally very expensive to produce. With current technology, these fuels cost anywhere from double to ten times more than petroleum-based fuels.

In terms of pollution effects, synfuels carry the same air pollution problems as conventional fuels, although the emissions of sulfur dioxide and sulfur trioxide are generally less. A serious concern is that continued dependence upon burning of fossil fuels, including synfuels from tar sands and coal, will increase the global carbon dioxide levels creating a world-wide "greenhouse" effect.

Solar power appears to offer many advantages. Solar power is abundant. Each year, over 10^{19} BTU of energy reaches the continental United States, several hundred times more than the projected power uses through the year 2000. Harnessing even a fraction of this energy could make a significant impact on the use of fossil or nuclear fuels.

The present technology for conversion of solar energy to useable energy does not bode well for solar energy to make an impact on energy usage in the near future. Photoelectric systems such as solar cells are low in efficiency and high in costs. Large power plants which use banks of computer-directed mirrors to focus the sun's energy to boil a liquid for use in a turbine system are highly complex and expensive. Of all of these systems, the only ones that seem to offer a potential for immediate application are the thermal hot water heaters for use on homes and apartment buildings.

Solar power has problems other than just cost. Most obviously, the sun's energy can only be captured during the day. At night, either an alternate power generating system must be used, or the electricity from the sun must be stored. For the quantities of energy required, no existing storage system can handle the load, although innovative hydrostatic, flywheel and battery energy storage devices have been proposed.

A further difficulty of solar power is that solar collectors are large. A collector which could make up the energy that the United States purchases from the Middle East each year would measure one mile by five thousand miles. Collectors of this scale would have to be placed in sparsely populated areas, preferably deserts, to avoid competition for sunlight with crops. This introduces the problem of transmitting enormous amounts of power over long lines, for which resistance losses significantly reduce the efficiency of the overall system.

One proposal which has been raised to deal with these problems is to use solar power to generate a fuel which can then be transported to a power plant near the users and converted to electrical power. For the fuel to be viable, it must be nonpolluting, easily transported and come from a cheap, abundant feed stock. The fuel most often suggested is hydrogen.

Hydrogen can be generated from water by electrolysis, transported through pipelines to a power plant and burned with oxygen to generate heat to run a conventional power plant. Alternately, the hydrogen and oxygen can be mixed in a fuel cell to generate electricity directly at the point of use. Unfortunately, the electrolysis of water is not a simple process and is actually inefficient because of the high overpotentials which must be applied to the electrodes. It would be far more efficient if a molecular species could be found which splits water (eq. 1, p. 6) directly using sunlight as its power source. The production of such a molecule is the long range goal of this research.

MOLECULAR HYDROGEN SOURCES

Balanzi, *et al*,¹ have listed eight requirements for any photochemical process which is intended for use in solar energy conversion. These are:

1. The absorption spectrum of the active molecular species should match the output spectrum of the sun as closely as possible. As the sun's maximum radiation is in the yellow region, compounds with the color complement of yellow such as blue, purple or green are best for solar energy conversion.
2. Upon absorption of light, the system must be able to undergo a chemical reaction which uses the energy of the captured light.
3. Following step 2, the system must be able to undergo further reactions to return to its starting condition. These further reactions may themselves be photochemical in nature, or may simply flow thermodynamically downhill. This allows the system to be cyclic.
4. The amount of usable energy produced per unit of light absorbed should be as large as possible.
5. At least one of the reactions which produce energy in the cycle must be able to be carried out under controlled conditions so that useful work may be obtained. This is a thermodynamic restriction which maximizes the recovered work.
6. The useful reaction should return as large a percent of the captured solar energy as possible.
7. The reactants and products of the useful reaction should be easily stored and transported.
8. The system should be as economical as possible. The liberation of hydrogen from water and the subsequent reformation of water through burning or fuel cells meets requirements 5, 6, 7 and 8. Requirements 1-4 establish a set of criteria for designing an appropriate molecular system.

Over the past decade, the search for a catalyst to evolve hydrogen from water has been underway. A lot of attention² has been given to the transition metal complexes due to the large and diverse chemistry these compounds have undergone when excited by the absorption of light.^{3,4}

There have been several theoretical schemes for the production of hydrogen from water or acidic solutions.

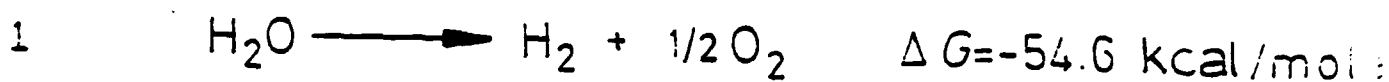
Scheme 1 involves the absorption of light by a metal species to produce the electronically excited state which can then react with a proton in solution leading to hydrogen evolution and oxidation of the metal species. This oxidized species can then react with water to produce the original metal species, oxygen and protons.⁵ Bolton has suggested that a scheme of this nature could be driven by light with a wavelength of 611 nm, or roughly 14% of the sun's output.⁶

A scheme to produce hydrogen from a solution of acid HX by metal halide complexes (MX_6) is shown in Scheme 2. When a metal halide species absorbs light to produce the excited state, it might be possible for one of the X species to transfer two electrons to the MX_5 unit, a process known as charge transfer. The resulting X^+ species would be very reactive and could react with an X^- from solution to form X_2 . The MX_5^- species would then react with a proton in solution to yield hydrogen and through further reactions return to its original MX_6 state. The overall reaction would be the formation of hydrogen and the halide, probably either chlorine or bromine, from the starting acid.

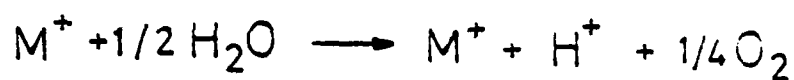
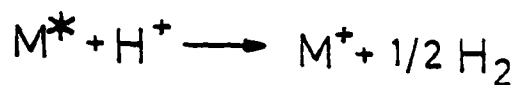
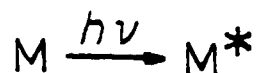
A final scheme is shown in Scheme 3.⁸ The first step involves protonation of the metal by water, followed by absorption of light to yield to the electronically excited state. In this excited state, a transfer of two electrons from the metal to the proton could occur, causing the proton to become negatively charged or hydridic. This species would then react with a proton in solution to yield hydrogen. The original metal species is now doubly oxidized and must be a powerful enough oxidant to react with water to return the metal species to its original state forming oxygen and protons. The key points of this scheme are that the original metal species must be basic enough to protonate in water (the first step) and that the oxidized metal species must be able to oxidize water (the last step). This is the scheme Dr. Bitterwolf and I are directing our efforts at in search of a water splitting catalyst.⁹

In Scheme 3, two electrons were transferred from the metal to the proton in the electronically excited state. The transfer of two electrons from a single species is not as energetically favorable as two species donating one electron each. For this reason, it appears to be more favorable to synthesize a catalyst containing two metal atoms to supply the necessary two electrons for each hydrogen molecule.¹⁰

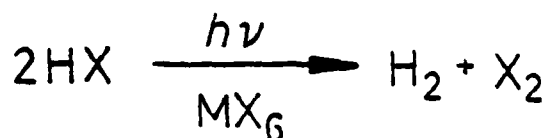
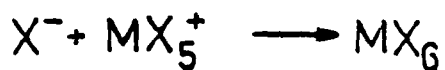
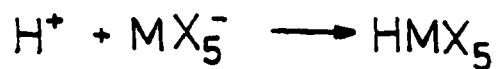
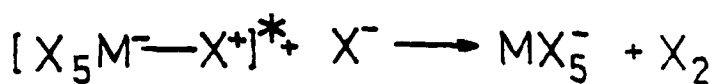
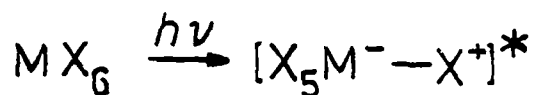
Further arguments for the use of double metal systems may be found in nature. There are several enzymes which are believed to have at their reaction sites two metal atoms (Figure 1, p.8). The enzyme involved in the water splitting step of photosynthesis, is believed to have two manganese atoms 2.9Å apart.¹¹ Nitrogenase, the enzyme which catalyzes the reduction of nitrogen to ammonia, appears to have at its reaction site a core of two molybdenum atoms which are held 3.668-3.306Å apart by three bridging sulfur atoms. Connected to each molybdenum atom is an

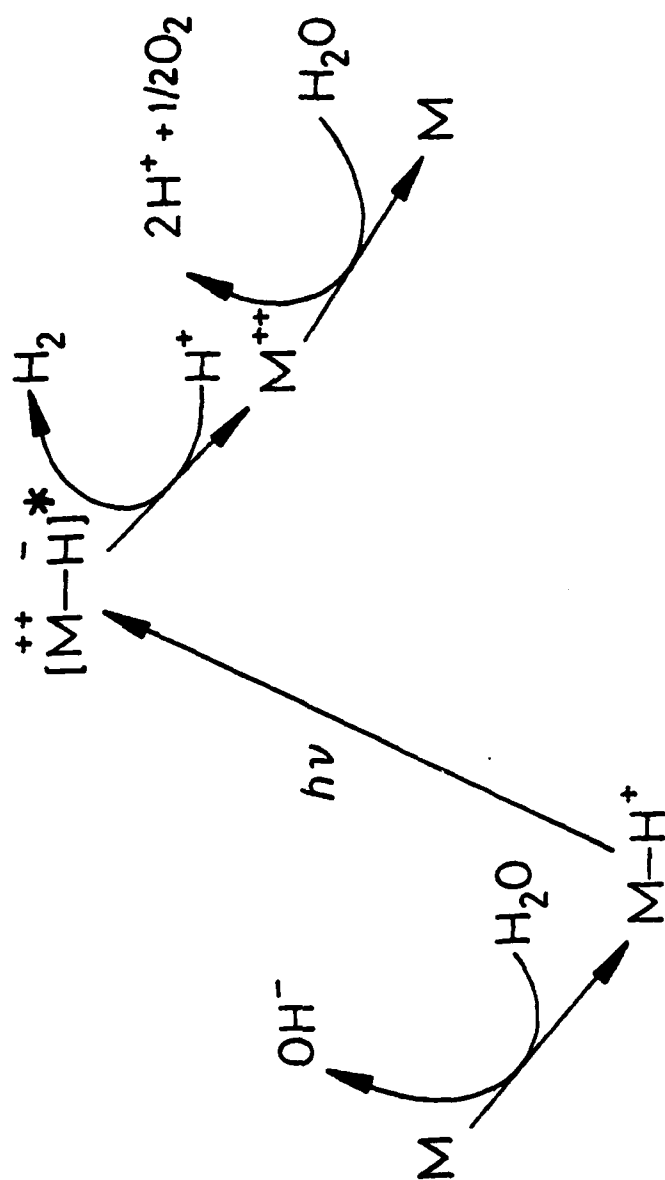


Scheme 1



Scheme 2



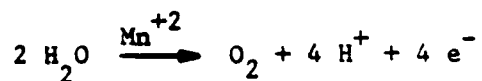


Scheme 3

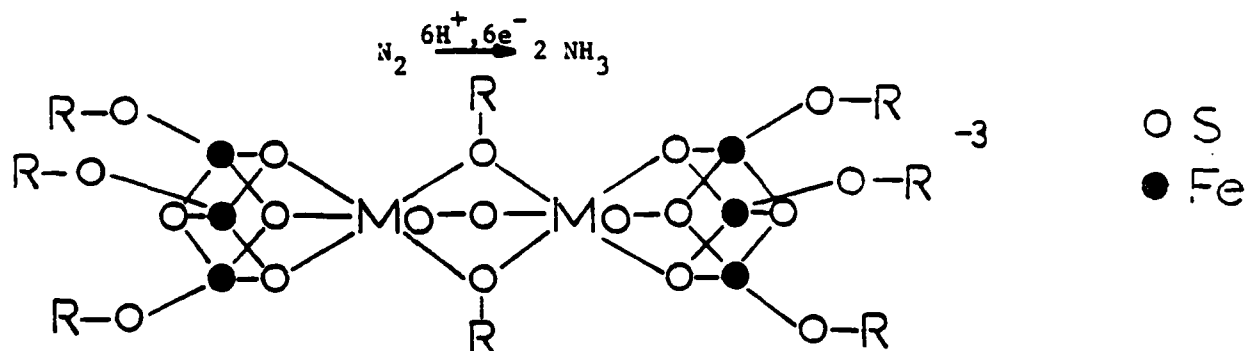
Fig 1

Double Metal Enzymes

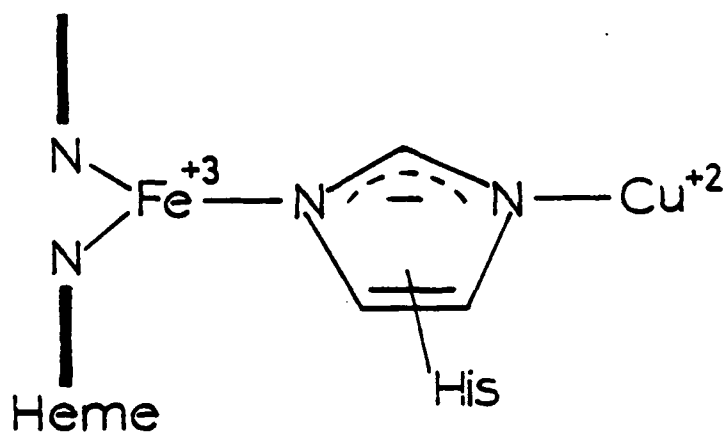
The enzyme used in splitting water into oxygen and protons appears to have two Mn atoms 2.9Å apart.



Nitrogenase has two Mo atoms 3.668-3.306 Å apart.



Cytochrome oxidase appears to have a Fe and Cu atom magnetically coupled by histidine.



iron sulfur cube, a structure which is believed to be involved in electron transfer.¹² The reverse reaction of water splitting, formation of water from oxygen and protons, is catalyzed by cytochrome oxidase, which has as part of its structure an iron and copper atom magnetically coupled by histidine.¹³

Tying this all together, the goal of our project is to develop a double metal system, capable of protonating in water and in a light-induced step generate hydrogen with reformation of the catalyst by the oxidation of water.

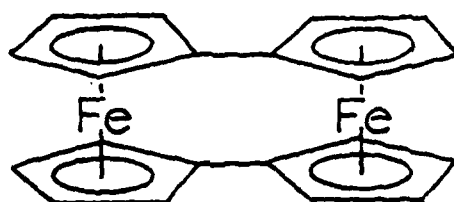
The concept of synthesizing double metal systems for hydrogen evolution was developed by Bitterwolf¹⁴ while studying ferrocene protonation in strong acids.¹⁵ During the course of this study it was determined that (1.1) ferrocenophane (II) evolved hydrogen from trifluoroboric acid (HBF_3OH). In this molecule, two iron atoms are held rigidly next to one another by the dicyclopentadienyl methane systems. With the iron atoms in this configuration, protons bonded to them can come within a critical distance to allow bond formation and evolution of hydrogen.¹⁶ This is in contrast to the behavior of biferrocenyl (IV) and diferrocenyl methane (V) which evolve hydrogen very slowly from trifluoroboric acid.¹⁵

This slow evolution of hydrogen compared to (1.1) ferrocenophane can be rationalized in terms of the position of the iron centers relative to one another. In IV and V, the protonated iron centers are free to rotate relative to one another, and hydrogen evolution occurs only when the two have rotated close enough for the protons to interact. In II, the two iron centers are already held rigidly close to one another, and this is reflected by the increased rate of hydrogen evolution.¹⁷ Thus, an important requirement of hydrogen evolving double metal systems is close proximity and a rigid geometry for the metal centers.¹⁸

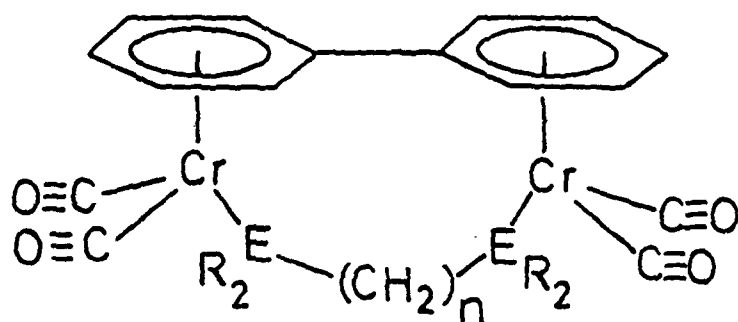
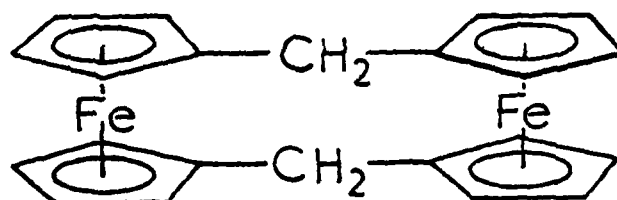
Recent work by Mueller-Westerhoff has shown hydrogen elimination from II to be catalytic if a suitable reducing agent, such as stannous chloride (SnCl_2), is present.¹⁹ (Scheme 4, p. 12). In this scheme, (1.1) ferrocenophane supplies the two electrons necessary for hydrogen evolution. The stannous chloride is then oxidized from Sn^{+2} to Sn^{+4} , reducing the oxidized (1.1) ferrocenophane back to its original state. This allows further reaction with acid, evolving more hydrogen. This cycle is continued until all of the SnCl_2 is oxidized.

Compounds I, II, and III have all been studied by Bitterwolf and are known to evolve hydrogen from super acid solutions^{16,20}. Bisfulvalene di-iron (I) readily evolves hydrogen from hexafluoro-antimonic acid. In the less active trifluoroboric acid, however, hydrogen evolution is almost undetectable. This can be explained by the close interatomic distances of the two iron atoms. When one of them becomes protonated, the positive charge helps repel attack by protons on the second iron

I

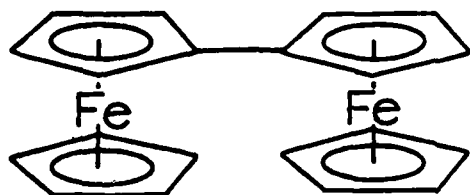


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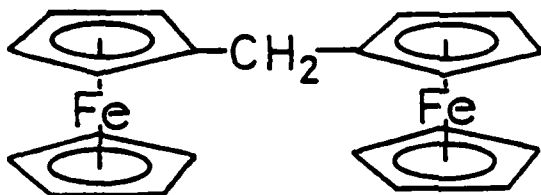


III

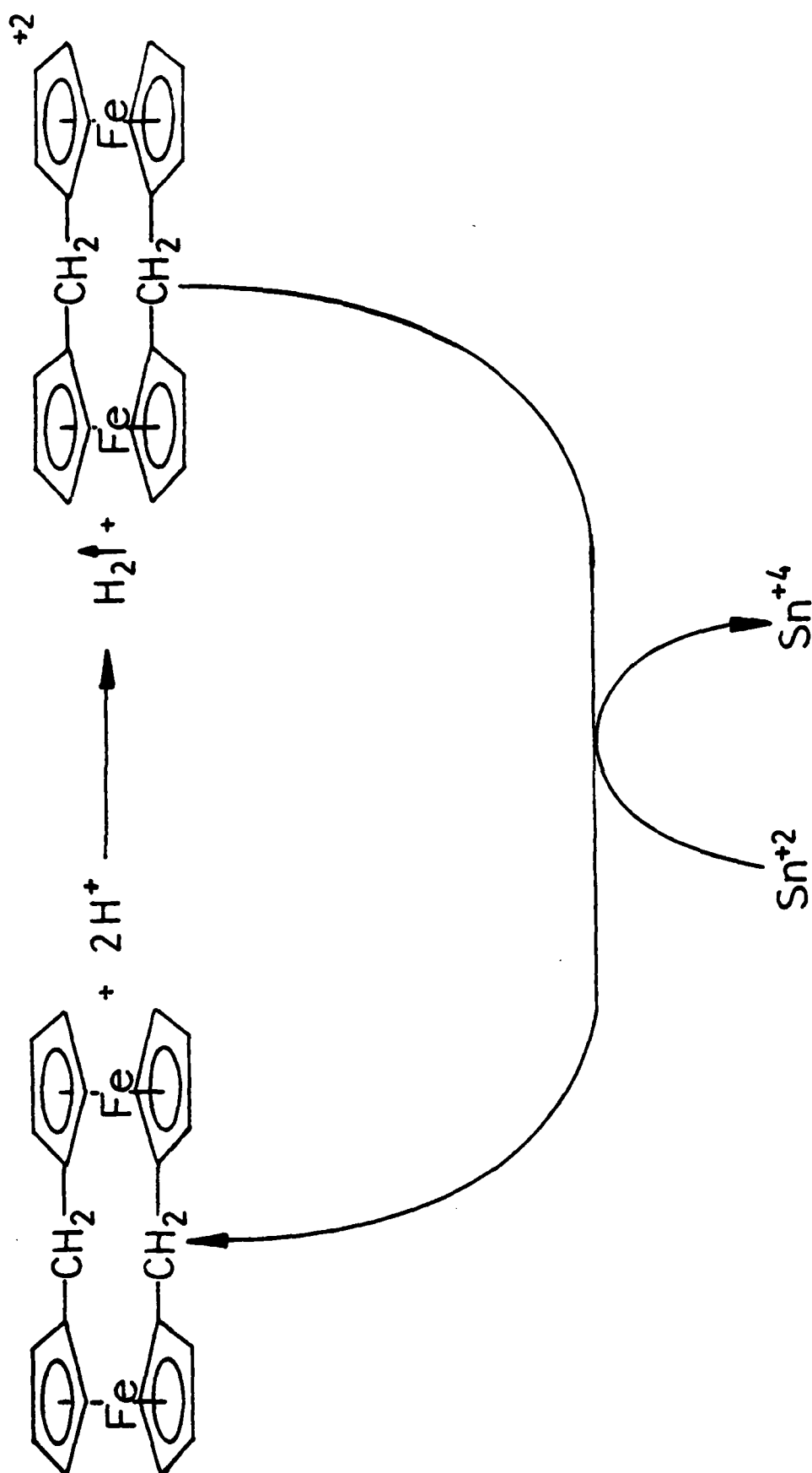
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IV



V

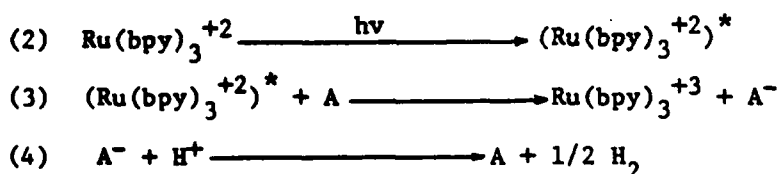


Scheme 4

atom, hence the need for the stronger acid. In II, the distance between the iron centers has been increased by the presence of methylene groups between the rings. This reduces electrostatic repulsion between the two metal centers and allows hydrogen evolution from the less active trifluoroboric acid.¹⁶ The presence of the methylene group also helps to electrically insulate the two metals from one another, whereas in I the developing positive charge on one iron atom may be communicated through the rings, decreasing the electron density around the second metal.¹⁸ In trying to develop systems which will evolve hydrogen from even less active solutions, such as trifluoroacetic acid (CF_3COOH), chromium dimers such as III have been prepared.²⁰ These compounds have been found to be more basic than II, but still require trifluoroboric acid for hydrogen evolutions. Further efforts towards developing more basic compounds are heading towards a preparation of dicyclopentadienyl cobalt dimers.²¹ Cobalt monomers exist which are known to protonate in methanol, a very weak acid.²² It is hoped that cobalt dimers will evolve hydrogen from weakly acidic solutions. Pursuit of research in this area will continue until double metal compounds are developed which will protonate in water.

Even though compounds I, II, and III evolve hydrogen from acid, none of them appear to have a light-induced step in the reaction sequence - a crucial consideration for photochemical evolution of hydrogen.

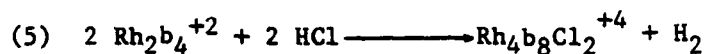
There are several other compounds, however, which do evolve hydrogen photolytically from acidic solutions under various schemes. An example of one such system is represented by the compound $\text{Ru}(\text{bpy})_2\text{3}^+$ (byp = 2,2' bipyridine).²⁴ In this scheme,²⁵ a charge transfer from the electronically excited $\text{Ru}(\text{bpy})_3^{+2}$ (2) to a suitable acceptor molecule, A (3) occurs producing A^- , a powerful reducing agent which can reduce protons as hydrogen (4).



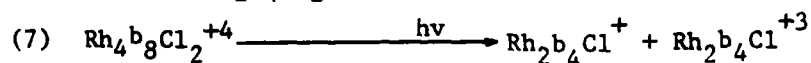
Gafney and Adamson have used $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$ as the acceptor molecule,²⁶ but the hydrogen production for this system is very slow.

An example of a bimetallic system which photolytically generate hydrogen from acidic solutions is the $\text{Rh}_2\text{b}_4^{2+}$ system (b=1,3-di-isocyanopropane) by Gray *et al.*²⁷ In degassed 12M HCl this compound was found to evolve hydrogen with 546 nm light, each rhodium center being oxidized from Rh (II) to Rh (III) to effect the two electron transfer necessary for hydrogen evolution.²⁸

The production of hydrogen was actually found to occur in two steps, the first a thermal reaction and the second a photo-chemical step.²⁹



The actual photolytic step appears to be the cleavage of the $\text{Rh}_4\text{b}_8\text{Cl}_2^{+4}$ cluster into two $\text{Rh}_2\text{b}_4\text{Cl}_2$ units.²⁵



Recently, a novel di-platinum hydride system (VI, VII) has been prepared by Geoffrey, *et al.* which produces hydrogen when irradiated with light of wavelength greater than 300 nm. The reaction occurs in acetonitrile (CH_3CN) over a course of 30 min to yield one mole of hydrogen per mole of complex. Analysis of the solutions after hydrogen evolution showed VI yielded VIII and VII yielded IX. The light source can be a U.V. lamp, a fluorescent light, or sunlight.

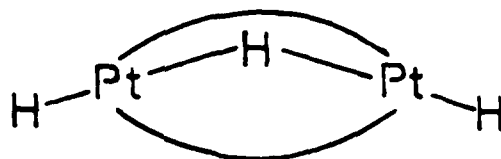
In the formation of hydrogen and oxygen from water, the intermediate formation of oxygen atoms, hydrogen atoms, or hydroxyl radicals should be avoided. Reasons for this are that these species are highly reactive and could easily destroy the catalyst. To overcome this, Balanzi, *et al.* have suggested using bimetallic systems in which the molecular geometry is suitable for the production of oxygen, hydrogen, or hydrogen peroxide without high energy intermediate species formation.³² Three examples are shown in Figure 2 (p. 16).

In the systems discussed above it has been shown that currently there are metal and di-metal systems capable of producing hydrogen, in some cases photolytically, from acidic solutions. There are not, however, any systems currently which can cyclically evolve hydrogen from water. As more and more metal systems are synthesized, chemists come closer to realizing this goal.

Project Approach

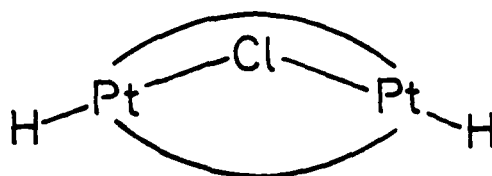
In choosing my Trident project, Dr. Bitterwolf and I decided to continue work on bi-metal systems. We hoped to synthesize compounds with novel chemical properties, to demonstrate the feasibility of such synthesis, and to study more about interactions between metal centers in the course of chemical reactions.

VI



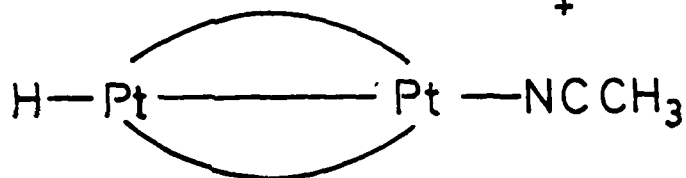
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VII



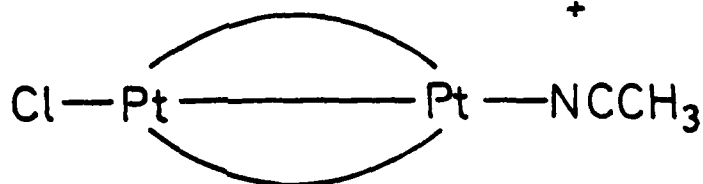
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IX



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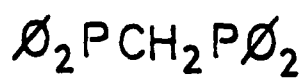
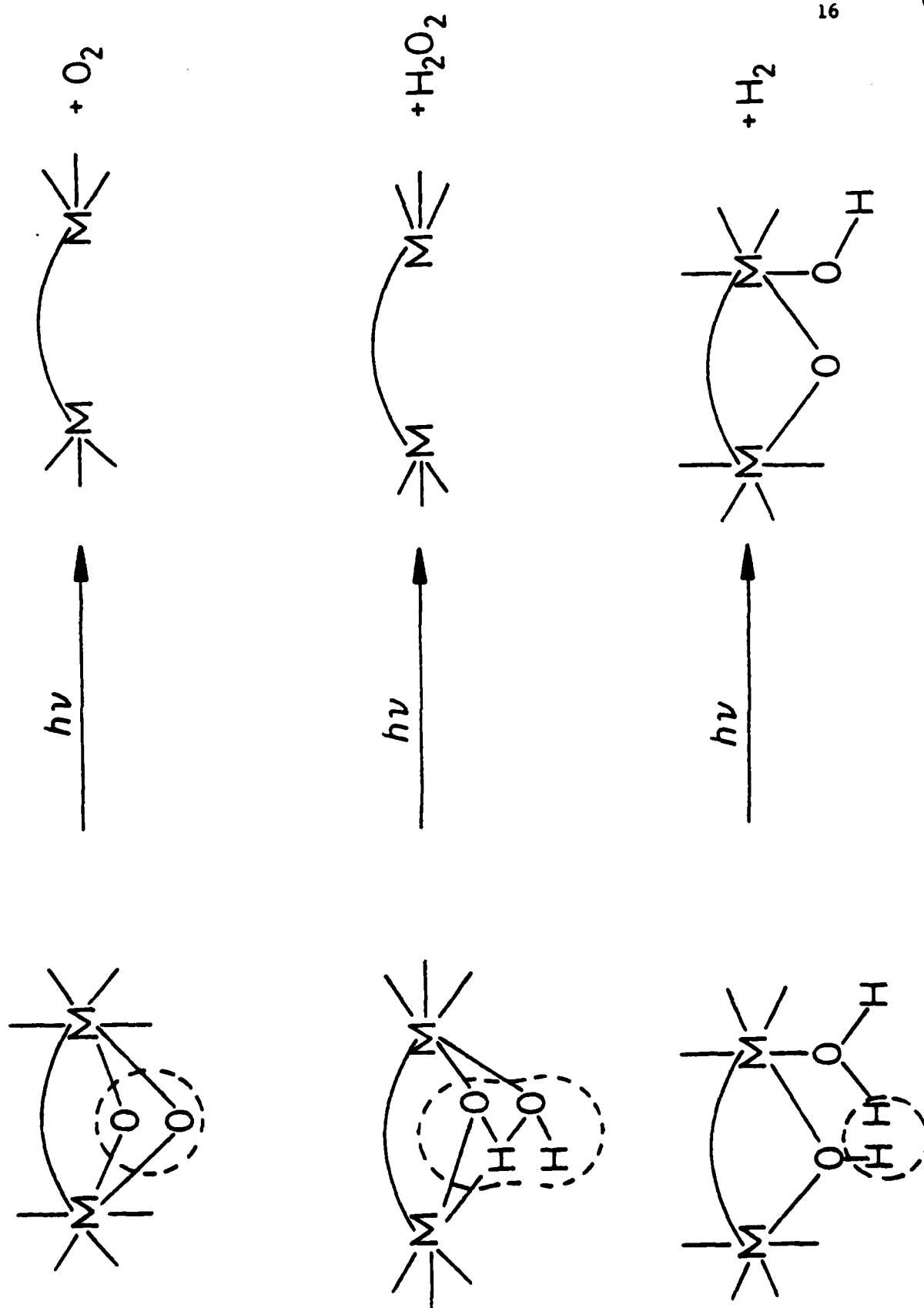


Fig 2



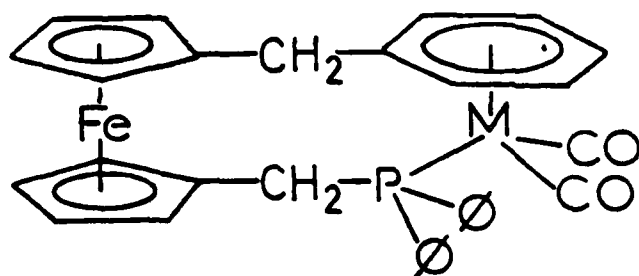
After consideration of several types of double metal compounds, we decided to focus our work on mixed metal systems, compounds in which dissimilar metal atoms are held at close interatomic distances in rigid configurations. This decision was based upon the scarcity of such systems and their potential for novel properties, such as light induced charge transfer between metal centers in the protonated state.³³ We were also interested in learning their hydrogen evolving abilities in acidic solutions, with the possibility for one of the steps in the reaction series being photo induced. The metals under consideration, Fe, Cr, Mo, W, as a general rule, form bright-colored complexes, increasing the likelihood of photo-induced reactions in the visible spectrum.

We decided to start with ferrocene (X, p. 23) as the backbone of the molecule. Electrophilic reactions of the molecule are well understood, allowing us to more easily approach the problem of placing ligating groups of the proper geometry onto ferrocene to incorporate a second metal. Ferrocene itself already has one of two metals in place, is stable under a wide range of reaction conditions, and has been used along with its derivatives extensively by Bitterwolf and myself over the past several years for other studies.

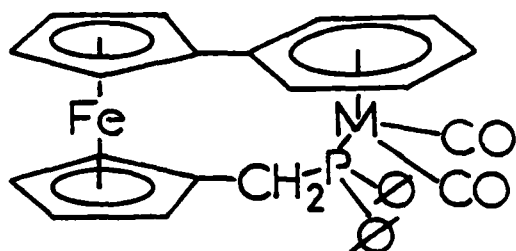
The series of compounds we originally planned to synthesize were of the general type XI and XII. In these complexes, the second metal (Cr, Mo, or W) is held rigid with respect to the iron center of ferrocene via an arene-metal complex and a methylene phosphine bridge. Systems of this type have never been synthesized.

In systems XI and XII, the effect on distance between the two metal centers can be studied. In XII, the second metal center is somewhat further away from the iron atom than in XI by the presence of a methylene group. This methylene group also serves to electronically insulate the cyclopentadienyl ring in ferrocene from the arene ring-metal complex.

The actual proposed structure of the molecule had to be modified. Dr. Bitterwolf had been trying to synthesize other molecules with phosphine groups and found them difficult to synthesize and purify. They were also very susceptible to air and moisture. It was decided that the second bridge system should be a phosphite group ($-\text{CH}_2\text{OP}_2$) due to its ease of synthesis and better air stability. In choosing which systems (XI or XII) to start with, previous experience with synthesizing benzylferrocenes was the critical factor. Chromium was chosen as a starting point for the metal M. Other chromium systems had the attractive properties of ease of synthesis, good yields, and air stability. Thus, the first compound I chose to synthesize was XIV.



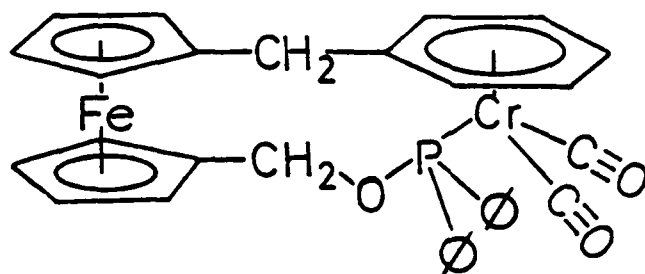
XI



XII

M = Cr, Mo, & W



XIV

Results

The synthesis of chromium 1-benzyl-1'-methyldiphenylphosphite ferrocene dicarbonyl (XIV, $M=Cr$, $Ar = -CH_2-C_6H_5$) required as a starting material for Scheme 5, 1-benzyl-1'-ferrocene carbinol, (XIII, $Ar = -CH_2-C_6H_5$) a compound which had not been previously synthesized.

Three different routes were tried to obtain XIII. The first reaction scheme, Scheme 6, (p. 22) had as a starting material trimethylammonium methyl ferrocenium iodide (XV).³⁴ This compound is known to undergo a displacement of trimethyl amine to yield the ferrocene carbinol in a refluxing solution of NaOH (eq. 8) in yields up to 79%. It was thus envisioned that the trimethyl amine group could serve as a protecting group for the alcohol, allowing the electrophilic addition of a benzyl chloride to the second ring via a Friedel-Crafts reaction with benzyl chloride to yield XVI. Subsequent formation of the carbinol (XIII) would then be accomplished by the reaction with NaOH. The overall reaction would then require two steps, holding the possibility for relatively high yields.

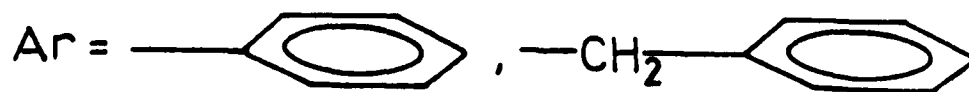
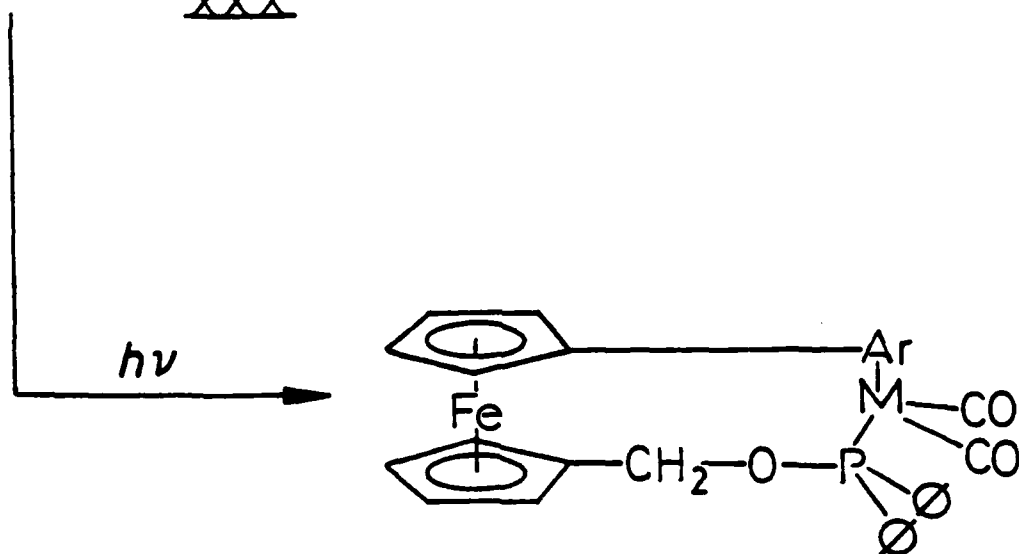
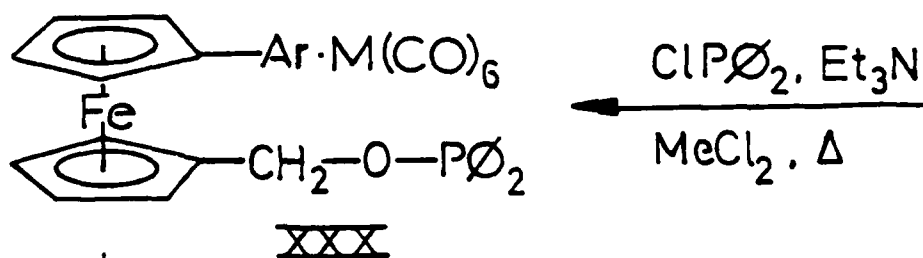
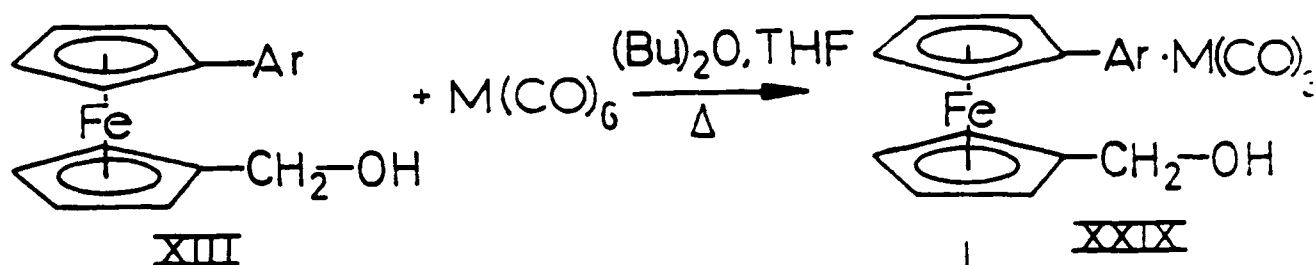
When the reaction sequence was first attempted, there was great difficulty in isolating any organic soluble material from the hydroxide reaction. After much effort, the product finally isolated proved to be the benzylferrocenyl carboxylic acid (XVII) in 50% yield.³⁶ This could be reduced to the carbinol with lithium aluminum hydride.

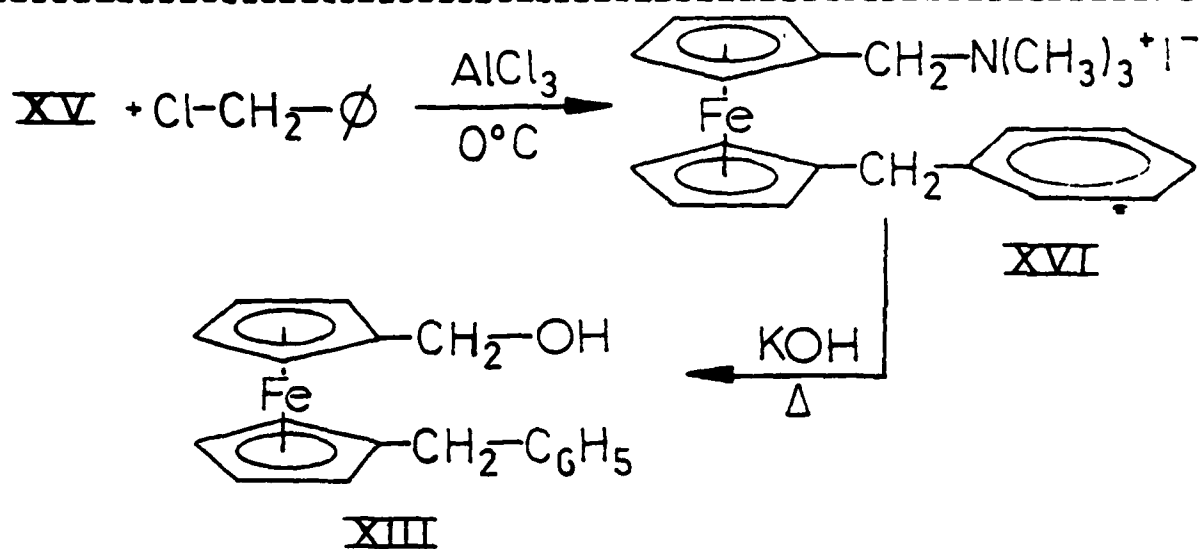
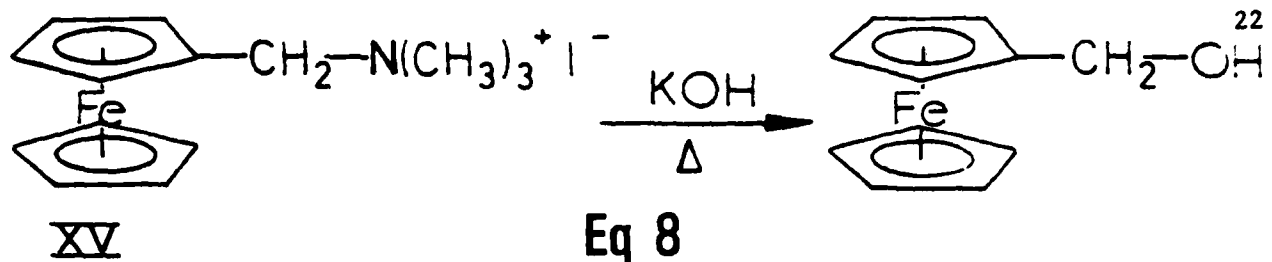
When the reaction was repeated in an effort to produce XVII, none of the acid XVII could be isolated.⁽¹¹⁾ Instead three brown oils were isolated. Their structures are unknown, but infrared and nuclear magnetic resonance data suggest that the amine group has been retained.

A second route to XIII is shown in Scheme 7 (p. 23). This route used methyl ferrocenecarboxylate (XX) as the starting point of the reaction. The electron withdrawing properties of the ester function serve to inhibit any electrophilic substitution reactions, such as Friedel-Crafts reactions, to the already substituted ring causing instead formation of the 1,1' compound. The ester function could then be reduced to the alcohol with lithium aluminum hydride ($LiAlH_4$). Methyl ferrocenecarboxylate (XX) could easily be formed via ferrocenecarboxylic acid (XIX), which was formed by the procedure of Biehl and Reeves.³⁷ First, o-chlorobenzoylferrocene (XVIII) is formed via a Friedel-Crafts reaction of ferrocene (X) and o-chlorobenzoyl chloride. The o-chlorobenzoyl group is then hydrolyzed by refluxing with potassium tert-butoxide ($K^+ t-BuO^-$) in 1,2 dimethoxyethane, and after acidification yields the acid (XIX) in greater than 85% yield. We were able to produce the acid (XIX) in 76% yield. The acid could then form the methyl ester after refluxing in methanol with a small amount of HCl present as a catalyst.

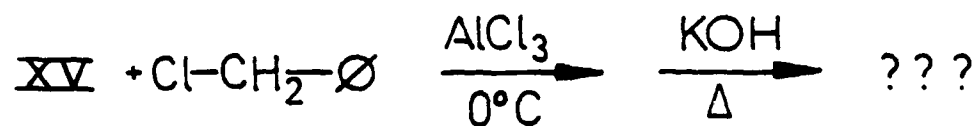
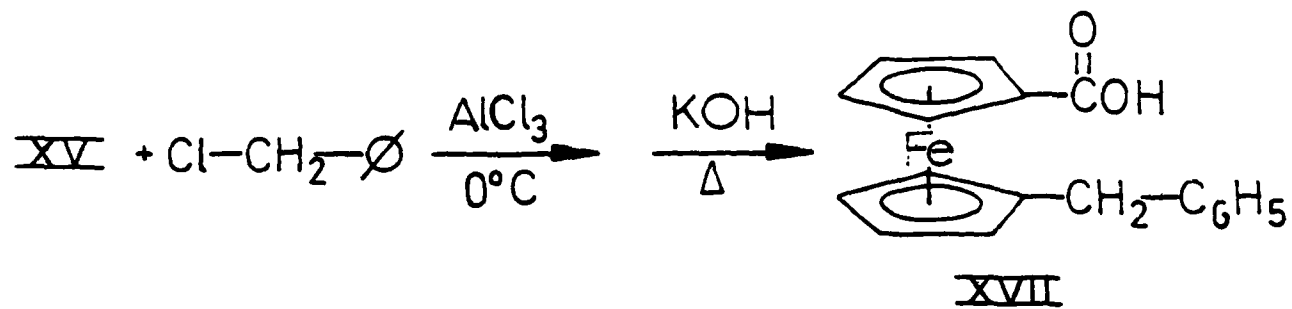
Scheme 5

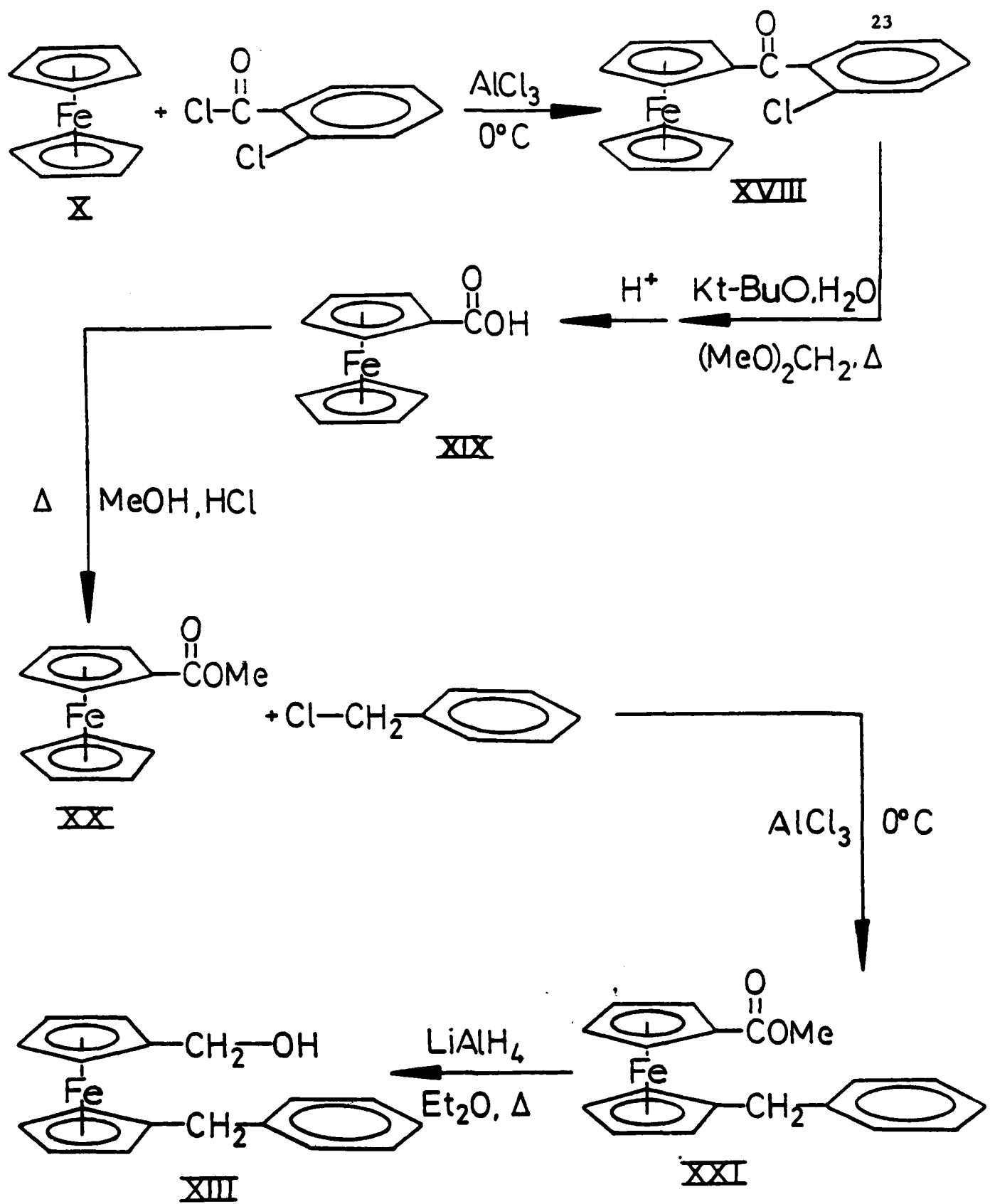
21





Scheme 6





Scheme 7

The next step was to form (XXI) via a Friedel-Crafts reaction of (XX) with benzyl chloride.^{38,39} Literature values for this reaction listed a yield of 81%. Lithium aluminum hydride reduction to yield the alcohol would then proceed essentially quantitatively. The reaction sequence thus had the potential for an overall yield of 69%. When the Friedel-Crafts reaction with benzyl chloride to yield (XXI) was carried out, however, a thin layer chromatogram (TLC) of the reaction mixture showed numerous components, including the product. Due to their poor resolution on the TLC, it was felt that purification of the components by column chromatography would be a futile effort. Instead, another scheme had to be developed to afford the benzyl carbinol (XIII) in high yields and in such a manner as to allow easy purification.

The scheme which was finally used is shown in Scheme 8 (p. 25). As can be seen, this route is essentially a rearrangement of scheme 7. The reaction sequence starts out with synthesis of benzoyl ferrocene (XXII) via a Friedel-Crafts reaction of ferrocene (X) with benzoyl chloride.⁴⁰ Benzoylferrocene was chosen vice benzyl ferrocene because previous work⁴¹ indicated we could form benzoyl ferrocene in higher yields than benzyl ferrocene. Also, the ketone group in benzoyl ferrocene serves to withdraw electrons from the top ring, forcing further electrophilic reactions to attack the bottom ring to form the 1,1' compound. The second step was the addition of the o-chlorobenzoyl group to the bottom ring by a Friedel-Crafts reaction³⁷ to yield the disubstituted compound (XXIII). The reaction was done in this order instead of forming the o-chlorobenzoyl ferrocene first, in order to maximize yields.

The effect on temperature on this reaction step is dramatic. During the addition of the aluminum chloride, the temperature is kept below 10°C. The reaction is then allowed to stir at 10°C for 40 minutes followed by stirring at room temperature for one hour.³⁷ If, however, the solution is then refluxed for 18 hours, the isolation of products is different, favoring formation of the 1,3-disubstituted compounds. (Figure 3, p. 26).

If the reaction is first carried out with benzoyl ferrocene and o-chlorobenzoyl chloride work-up of the reaction after refluxing showed 60% of the product to be the 1,3-disubstituted compound (XXIIIa) and 40% of the 1,1'-disubstituted compound (XXIII). If refluxing is omitted, virtually none of the 1,3 compound is formed. If the reaction is carried out with benzyl ferrocene, work up after refluxing yielded 80% of the 1,3-disubstituted compound (XXIVa) and 20% of the 1,1'-disubstituted compound (XXIV). This difference in the ratio of products can be attributed to the difference in ring electron densities of the benzoyl and benzyl ferrocene.

Scheme 8

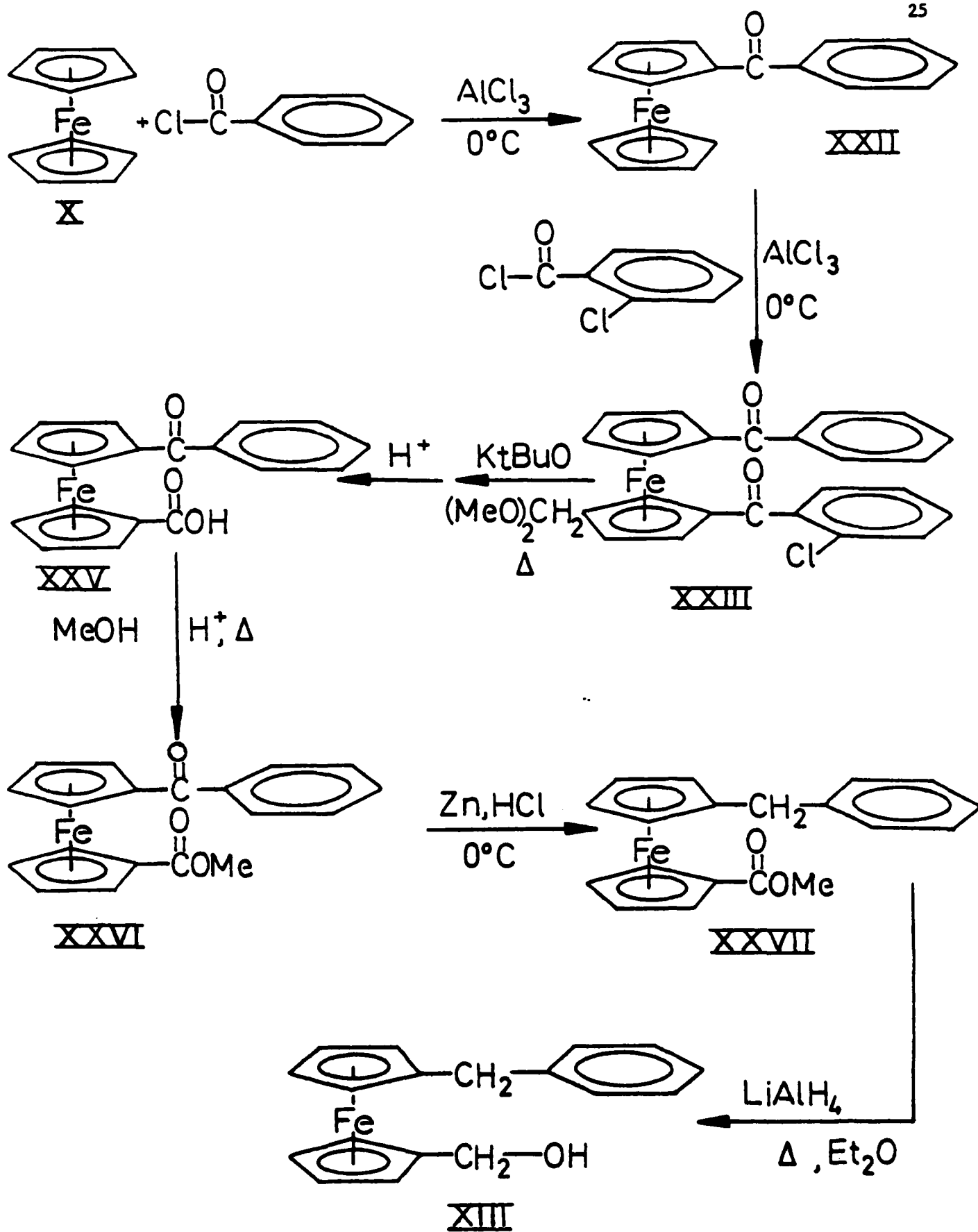
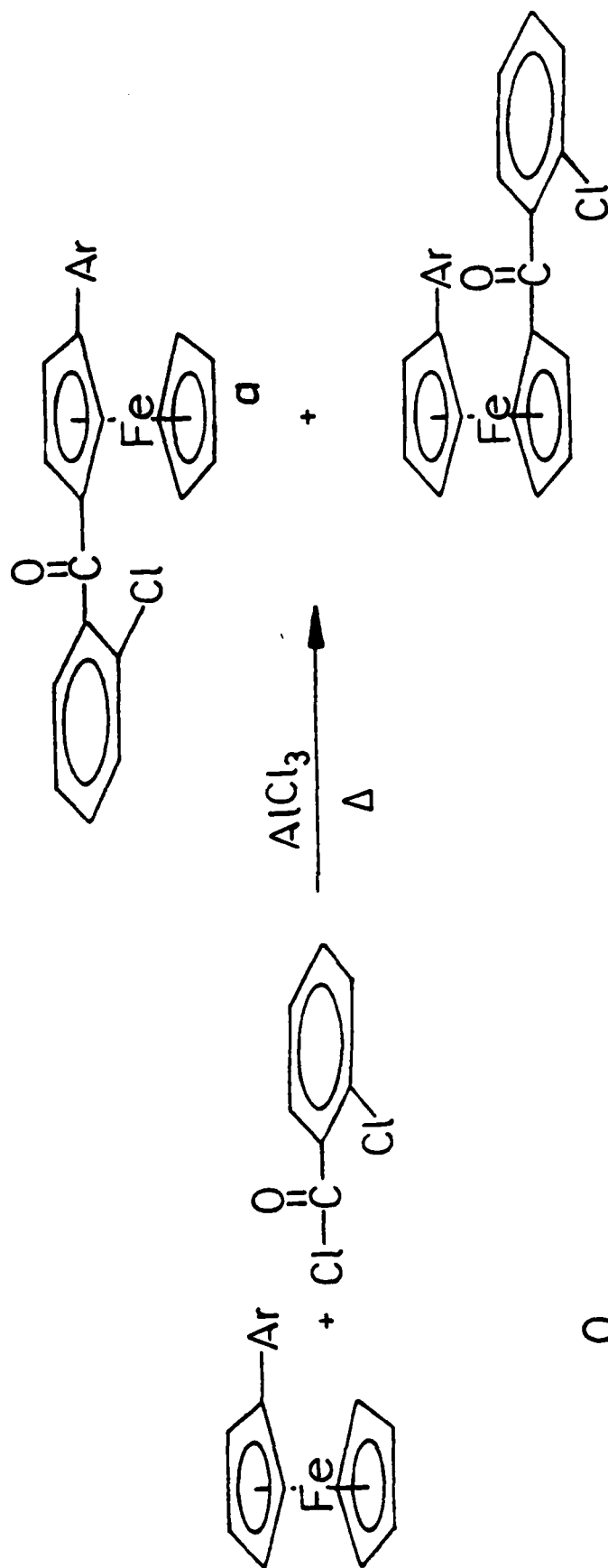


Fig 3



In the case of benzoyl ferrocene, the presence of the ketone serves to withdraw electrons from the cyclopentadienyl ring and facilitate formation of the 1,1'-disubstituted compound (XXIII). With benzyl ferrocene, the benzyl group has a slight electron donating effect, causing increased electron density in the cyclopentadienyl ring and hence favoring formation of the 1,3-disubstituted compound (XXIVa).

The mechanism of formation of the 1,3-disubstituted compound is interesting. A question arises as to whether or not the 1,1'-disubstituted compound is formed first (as in the reaction without refluxing) and then continued heating in the presence of AlCl_3 causes transfer of the group on the bottom ring to the top ring, or that formation of the 1,3-disubstituted compound proceeds directly. Experiments are under way in our laboratory to determine this.

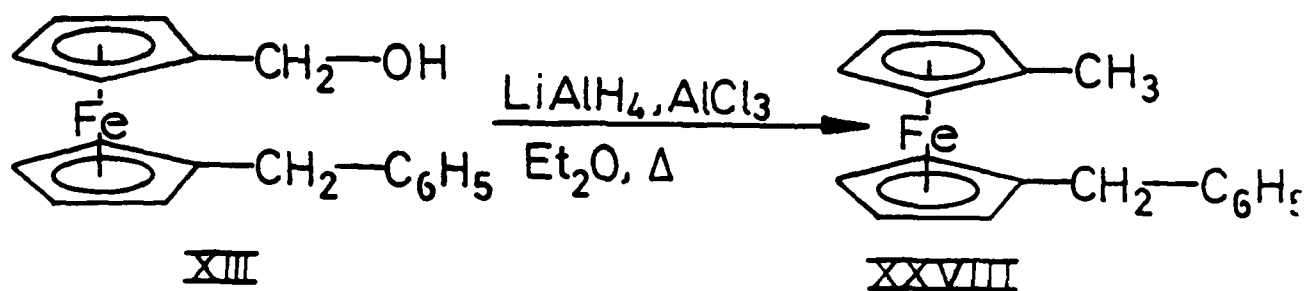
Once 1-benzoyl-1'-o-chlorobenzoyl ferrocene (XXIII) had been synthesized and isolated, the next step was to hydrolyze the o-chlorobenzoyl group with potassium tert-butoxide and isolate the 1-benzoyl ferrocene carboxylic acid (XXV). This was formed into the ester (XXVI) by refluxing in methanol with a trace amount of HCl present.

The fifth step was to form 1'-benzyl methyl ferrocenyl carboxylate (XXVII) from 1'-benzoyl methyl ferrocenyl carboxylate (XXVI), which required reducing a ketone in the presence of an ester. This was accomplished by a Clemmenson reduction (Zn , HCl) in ether at 0°C . The resulting compound, 1'-benzoyl methyl ferrocenyl carboxylate (XXVII) matched up with the product from the Friedel-Craft reaction in Scheme 7 by thin layer chromatography. The resulting ester was then reduced with an excess of LiAlH_4 in ethyl ether and purified by silica gel column chromatography. The resulting compound (XIII) was a bright yellowish-orange oil. The compound was identified by infrared spectroscopy and PMR (proton magnetic resonance). Of interest is the medium absorption at 3550 cm^{-1} in the I.R. which might correspond to an interaction between the alcoholic proton and the electron cloud of the benzene ring of the benzyl group. Synthesis of the corresponding 1'-phenylferrocenylcarbinol would allow a better configuration for interactions of this type. Lack of a methylene group between the ferrocene and the phenyl ring as in 1'-benzylferrocenylcarbinol would allow for the proton to sit more directly over the center of the phenyl ring. Experiments to determine this are currently underway in our laboratory.

In order to determine the mass of the alcohol, the compound was first reduced to 1-methyl-1'-benzylferrocene (XXVIII) with lithium aluminum hydride and aluminum chloride (Scheme 9) to facilitate easier movement through the gas chromatograph of the gc/mass spectrometer. An I.R. of (XXVIII) showed the complete absence of any O-H stretches and the PMR showed the disappearance of the singlet corresponding to the

Scheme 9

28



methylene group attached to the alcohol function and the appearance of a methyl group. Figure 4 shows a parent peak at 290.2, which corresponds to the theoretical mass of (XXVIII). Based on this evidence it was concluded that XIII had been produced.

The overall yield of (XIII) based on the starting ferrocene was 16.5%. The cause of the low yield is not known. However, the yield after the first two steps was 90.2%, and the reduction by LiAlH_4 is assumed to be quantitative. Since esterifications are typically high yield processes, the two low yield steps must be the hydrolysis and/or the Clemmenson reduction. A low yield for the hydrolysis reaction might be due to the steric bulkiness of the molecule which could prevent attack by the tert-butoxide anion.

With 1'-benzylferrocene carbinol (XIII), the addition of the second metal could proceed according to Scheme 5 (p. 31). The addition of the $\text{Cr}(\text{CO})_3$ was accomplished by refluxing (XIII) with an equimolar ratio of $\text{Cr}(\text{CO})_6$ in dibutyl ether for 12 hours.⁴² After cooling and removal of the dibutyl ether, addition of benzene formed a tan brown precipitate. This was collected by filtration and saved. A TLC of the benzene soluble phase showed seven components without any recovery of the starting alcohol.

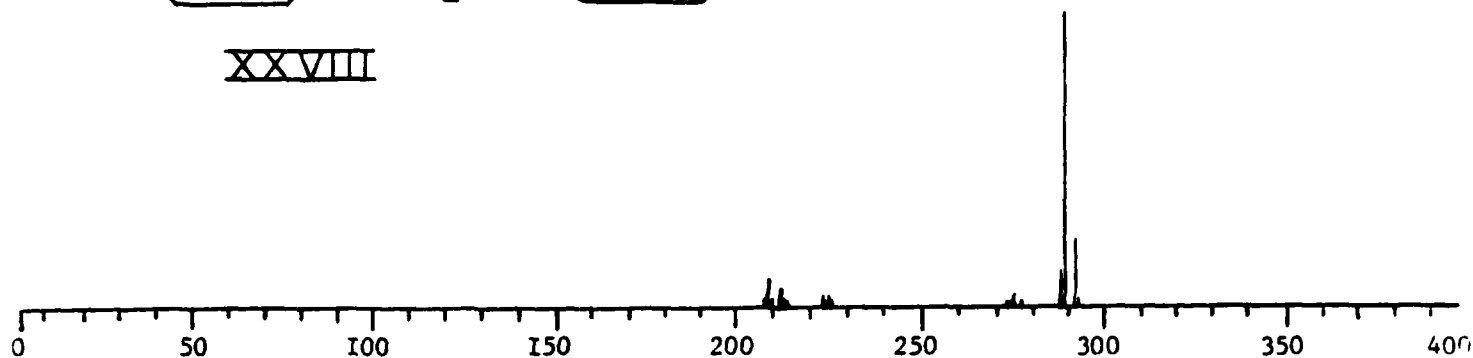
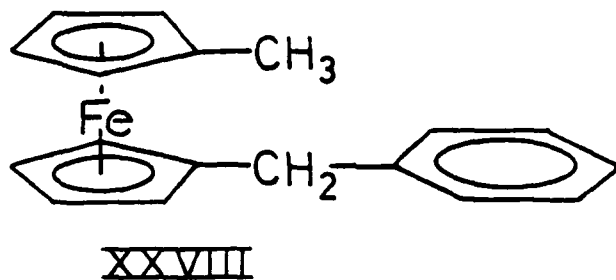
An IR of the crude mixture showed carbonyl stretches around 1970 cm^{-1} and 1890 cm^{-1} , indicative of arene-bound metal tricarbonyls. However, as purification proceeded by silica gel column chromatography, the successive IR's showed loss of the chromium. The only components of the mixture which could be identified were ferrocene carboxylic acid and 1'-benzylferrocene carboxylic acid.

An IR of the tan solid, however, showed it to be (XXIX, $\text{Ar}=\text{CH}_2-\text{C}_6\text{H}_5$, $\text{M}=\text{Cr}$) The compound proved to be insoluble in all common organic solvents and water, so that PMR was not possible. Other arene chromium tricarbonyls synthesized in our lab were bright yellows or oranges, and soluble in benzene.⁴³ The yield of this step was 8.9%, low for most of chromium reactions.

In order to see if refluxing in the presence of $\text{Cr}(\text{CO})_6$ was sufficient to oxidize ferrocenyl carbinols to acids, ferrocenyl carbinol was refluxed with $\text{Cr}(\text{CO})_6$ in dibutyl ether for 12 hours. Upon workup, most of the ferrocenyl carbinol was recovered (70%) along with a small portion of ferrocenyl monoaldehyde. Thus, it is possible for some oxidations to occur in the current scheme.

Fig 4

30



Base Peak = 290.2

Lower Abundance Cutoff Level = 4.0%

<u>Mass</u>	<u>Abundance</u>	<u>Mass</u>	<u>Abundance</u>	<u>Mass</u>	<u>Abundance</u>
208.1	7.5%	288.2	8.1%	291.2	22.2%
211.1	5.1%	290.2	100.0%		

GC Conditions:

Injection Port Temp. = 200°C

Column Temp. = 180°C

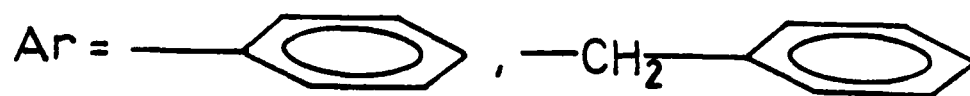
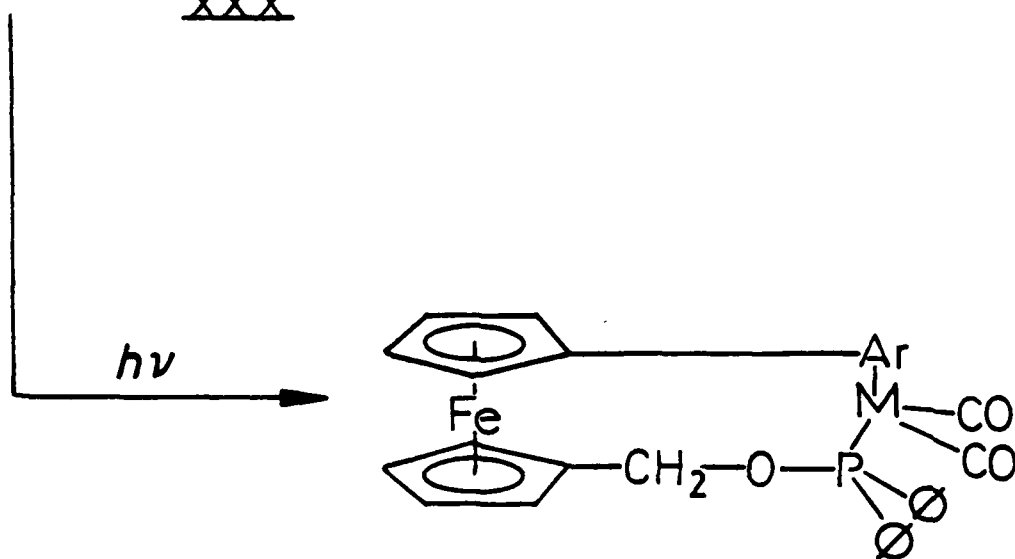
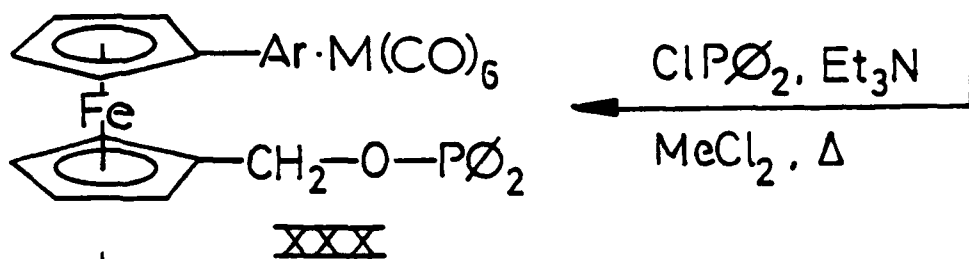
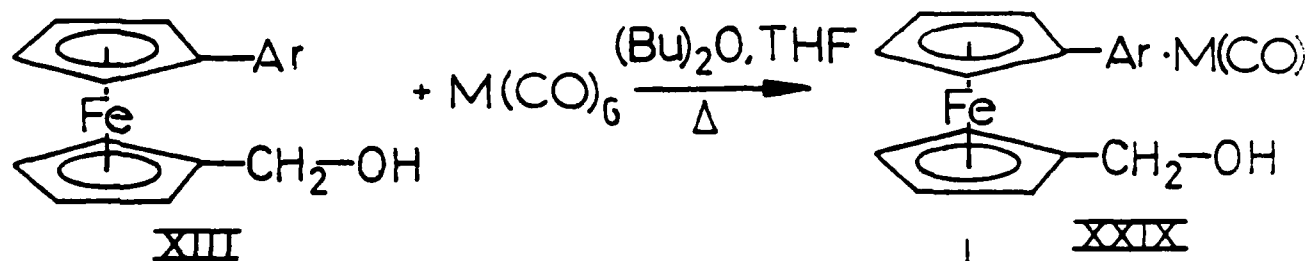
Carrier Gas Flow Rate = 30 ml/min

Column = 4mm (ID)x3ft (L) 2% OV101 & 2% Carb 20M on Chromosorb WHP

Retention Time = 2.3 min.

Scheme 5

31



$\text{M} = \text{Cr, Mo, W}$

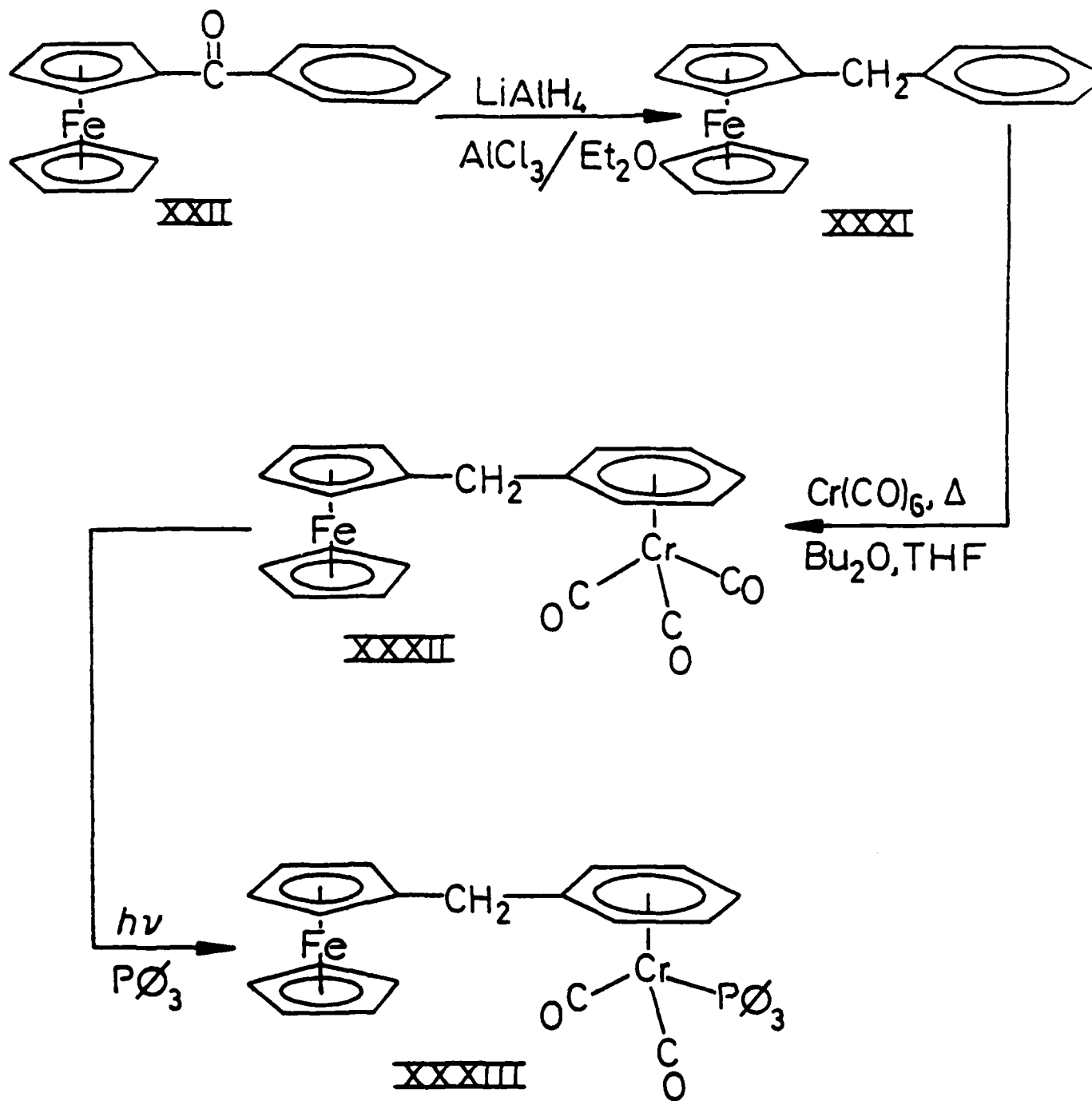
The next step involved formation of the phosphite (XXX) which was accomplished by refluxing the compound in dry methylene chloride with equimolar amounts of chlorodiphenylphosphine and triethylamine for four days.⁴³ After cooling, unreacted (XXIX) was filtered. The phosphite (XXX) was isolated by precipitation from a benzene/hexane solution. A tan precipitate formed and was filtered. A ^{31}P NMR of the solid showed a singlet at (sigma value) 43.2 upfield of phosphoric acid. An IR of the compound still showed the presence of chromium. Not enough of the compound, however, could be dissolved to obtain a PMR. This is the current status in the synthesis of (XIV).

Concurrently, other compounds have been synthesized which are chemically close to (XIV), but in which the chromium atom is not rigid with respect to the iron center. In this way, the importance of stereorigidity on the properties of the double metal systems could be investigated. Such a compound is benzylferrocene chromium dicarbonyl triphenylphosphine (XXXIII). The synthesis of (XXXIII) is shown on Scheme 10.

Benzyl ferrocene (XXXI) was obtained by LiAlH_4 reduction of benzoyl ferrocene (XXII). Benzylferrocene chromium tricarbonyl⁴⁴ (XXXII) was produced in the methods described previously after refluxing for four days. After removal of the dibutyl ether, the compound was extracted with hot hexane. The remaining mustard yellow powder showed the characteristic carbonyl absorption in the IR. However, the compound decomposed too rapidly in solution to obtain an PMR. The phosphine (XXXIII) was produced by irradiating a benzene solution of (XXXII) and triphenyl phosphine. After purification, the resulting orange oil showed a singlet at (sigma value) 91.37 upfield of phosphoric acid in the ^{31}P NMR and better stability in solution. This compound had not been previously synthesized.

Scheme 10

33



Experimental

Chemicals used were obtained from Aldrich, Strem, and Fischer Scientific and used without further purification. Solvents were obtained from Aldrich, Fischer Scientific, and Matheson, Coleman, and Bell. Dry methylene chloride was obtained by distilling methylene chloride which had been dried over sodium sulfate and filtering through a column of molecular sieves. Dry benzene was obtained by distilling benzene over calcium hydride under nitrogen and storing under nitrogen until used.

IR spectra were collected on a Perkin Elmer 467 grating spectrophotometer. IR of solutions were done with a Beckman 0.1 mm path length NaCl liquid cell. Mass spectra were obtained on a Hewlett-Packard System 5992 GC/MS fitted with a 4 mm x 3 ft glass column filled with 2% OV101 and 2% Carb 20M on Chromosorb WHP. PMR were collected on the Varian A-60A NMR and ³¹P NMR were collected on the Varian 80 MHz FTNMR. Melting points were determined on a Hoover melting point apparatus.

Benzoylferrocene (XXII)- A 3-neck 500 ml flask fitted with two glass stoppers, a condenser and a spin bar was flushed with nitrogen and charged with 150 ml of methylene chloride, 20.0g of ferrocene (.1076 moles), and 13.8 ml of benzoyl chloride (.1184 moles). The system was cooled to 0°C with a salted ice bath. 15.8g of AlCl₃ (.1184 moles) was slowly added, keeping the temperature below 10°C. After all of the AlCl₃ had been added, the solution was allowed to stir at 0°C for 1 hr. and at room temperature for 1 hr. 300 ml of 20% K₂CO₃ was slowly added. This solution was allowed to stir for several hours to destroy any residual AlCl₃ and benzoyl chloride. The methylene chloride layer was separated and washed with 2 100-ml portions of saturated NaCl and dried over MgSO₄. The methylene chloride was removed in vacuo and the product recrystallized from cyclohexane. 29.93 g of benzoylferrocene (95.91% yield) was recovered as dark red needles. M.P.: 106-107 C Lit. M.P.: 108.1-108.3°C.⁴⁵ IR (#2): 3095 (m), 3063 (m), 2915(w), 1787(w), 1718(w), 1634(s, broad), 1600(s), 1580(s), 1490(m), 1453(s), 1437(s), 1412(m), 1394(m), 1376(s), 1355(m), 1333(s), 1315(s), 1304(s), 1282(s), 1178(m), 1173(s), 1168(s), 1100(m), 1044(s), 1021(s), 1000(s), 947(s). NMR (#2): (sigma values) 4.21(s,5), 4.57 (t, J=1.5 Hz, 2), 4.92 (t, J=2 Hz, 2), 7.54 (m,3), 7.92 (m,2).

1-benzoyl-1'-(o-chlorobenzoyl) ferrocene (XXIII)- A 3-neck 500 ml flask was fitted with two stoppers, a condenser and a spin bar and was flushed with nitrogen. The flask was charged with 29.45g of benzoylferrocene (.1065 moles) and 100 ml of methylene chloride. The solution was cooled to under 5°C and 14.2g of AlCl₃ (.1065 moles) was slowly added, maintaining the temperature below 10°C. 13.51 ml of o-chlorobenzoyl chloride (.1067 moles) was added to the cooled solution. 14.23g (.1067 moles) of AlCl₃ was slowly added, maintaining the solution below 10°C. After the addition was completed, the solution was allowed to stir at 0°C for 1 hr. and then at room temperature for 1 hr. After completion of the

of the reaction, 100 ml of H_2O at $0^\circ C$ was slowly added, followed by 150 ml of 20% K_2CO_3 . This was allowed to stir overnight to destroy any of the unreacted $AlCl_3$ and acid chloride. The methylene chloride layer was separated and washed with 2 100 ml portions of saturated NaCl solution and then dried over $MgSO_4$. The methylene chloride was removed in vacuo and the product purified by column chromatography of four equal portions of the product on silica gel eluted with benzene. After removal of the solvent, 41.08g (94.41% yield) of the compound was recovered as a cherry red oil. IR: 3100(w), 3080(w), 3050(w), 2975(m), 2900(m), 1735(s), 1645(s), 1610(m), 1450(s), 1378(m), 1350(m), 1293(s), 1110(w). NMR: (sigma values) 4.23(s), 4.32(s), 4.60(q, $J=2Hz$), 4.75(t, $J=2Hz$), 5.0 (t, $J=1.5Hz$), 7.41(s), 7.56 (q, $J=1.8Hz$), 7.82(m).

1-benzoylferrocenecarboxylic acid (XXV)- A 3-neck 500 ml flask fitted with two stoppers, a condenser, and a spin bar was flushed thoroughly with nitrogen. The flask was charged with 107.7g (.96 moles) of potassium tert-butoxide, 225 ml of dimethoxymethane, and 4.84 ml of H_2O (.269 moles). 40.40g of 1-benzoyl-1'-(o-chlorobenzoyl) ferrocene (.0942 moles) was slowly added and the reaction allowed to reflux overnight, during which time the solution changed from a dark brown to a dark yellow in color. After refluxing, the solution was allowed to cool and then poured into a flask of 500 ml of H_2O . This was extracted with methylene chloride until no further material was extracted. The methylene chloride was then discarded. The H_2O layer was acidified with HCl until the solution was shown to be acidic by pH paper. At this point, the solution changed from a dark yellow to a cloudy brown color. The solution was extracted with ether until no further material was removed. The ether layers were combined and washed with 150 ml of H_2O and dried over $MgSO_4$. The ether was removed in vacuo resulting in a dark brown oil. Attempts to crystallize it failed, so the material was used without further isolation. IR: 3450(m, broad), 3410(m), 3090(m), 1700(m), 1645(s, broad), 1620(m), 1456(s), 1430(s), 1400(s), 1303(s), 1045(m).

1'-benzoyl methyl ferrocenylcarboxylate (XXVI)- The product from the above reaction was dissolved in 200 ml of methanol and placed in a 300 ml single neck flask fitted with a spin bar and a condenser. The flask was flushed thoroughly with nitrogen and 2 ml of conc. HCl was added as a catalyst. The solution was allowed to reflux overnight. After cooling, the solution was poured into a flask containing 500 ml of cold H_2O and neutralized with 20% K_2CO_3 . The solution was extracted with methylene chloride until no further material was taken up in the methylene chloride layer. The extracts were combined and washed with 150 ml of saturated NaCl solution. The methylene chloride extracts were dried over $MgSO_4$ and the solvent removed in vacuo. The product was a dark, sweet smelling oil. This was dissolved in petroleum ether and filtered. The filtrate was collected and the solvent removed in vacuo. The resulting product was a dark oil and was used without any further isolation.

1'-benzyl methyl ferrocenylcarboxylate (XXVII)- a 3 neck 500 ml flask was fitted with a glass stopper, a condenser, a gas inlet tube and a spin bar. Into the flask was placed 16.23g of the crude ester (XXVI), 250 ml of anhydrous ether, and 14.0g of granular zinc (.214 moles). The system was flushed thoroughly with nitrogen and cooled to 0°C with a salted-ice bath.⁴⁶ The necessary HCl (1.067 moles) was generated by placing 62.36g (1.067 moles) of NaCl into a 250 ml side-neck flask fitted with a spin bar and a separatory funnel. The side neck arm was connected to the gas inlet tube of the 3 neck flask with Tygon tubing and the end of the inlet tube was placed below the surface of the ether. The 250 ml flask was flushed thoroughly with nitrogen and 59.3 ml (.534 moles) of conc. H_2SO_4 was added to the separatory funnel. The acid was allowed to drop onto the NaCl slowly over a 5 hour period. After addition of the H_2SO_4 was complete, the ether solution was allowed to stir for an additional hour to ensure completion of the reaction. 150 ml of 20% K_2CO_3 was slowly added to the ether to neutralize any HCl remaining in solution, followed by an additional 100 ml of H_2O . The ether layer was collected, washed with 50 ml of H_2O , dried over MgSO_4 and the solvent removed in vacuo. The resulting orange oil was columned on silica gel eluted with benzene-methylene chloride (1:1). 12.3g (.0367 moles) of the product was recovered as a reddish oil. IR: 3080(w), 3020(w), 2948(m), 2865(s), 1750(s, broad), 1593(m), 1496(m), 1465(m), 1438(m), 1376(m), 1300(s), 1280(s), 1256(s), 1193(s), 1140(s).

1'-benzylferrocene carbinol (XIII)- A 250 ml Schlenk flask was fitted with a spin bar, condenser and flushed thoroughly with nitrogen. The flask was charged with 4.0g (.105 moles) of LiAlH_4 and 100 ml of anhydrous ether. 11.8g (.035 moles) of the above ester was added to the flask and the reaction was allowed to reflux for 1 hr. After cooling, 3 ml of ethyl acetate, 3 ml of methanol, and 50 ml of H_2O are added slowly to destroy any unreacted LiAlH_4 . The ether layer is collected and washed with 50 ml of H_2O . The ether layer is dried over MgSO_4 and the solvent removed in vacuo. The resulting oil is columned on silica gel eluted with benzene-methylene chloride (1:1). After solvent removal, 5.42g (16.45% yield based on starting ferrocene) of the benzyl carbinol was recovered as a yellowish-orange oil. IR(#3): 3600(s), 3550(m), 3430(s), 3084(s), 3060(m), 3030(s), 2930(s), 2875(m), 1946(s), 1886(s), 1603(m), 1495(s), 1452(s), 1442(s), 1407(m), 1385(s), 1294(w), 1232(m), 1194(w), 1121(w), 1100(w), 1050(s). NMR (#3): (sigma values) 3.69(s, 2), 4.12(t, 8), 4.32 (s, 1.33), 4.75(s, 1.5), 7.28(s, 6.2).

1-methyl-1'-benzylferrocene (XXVIII)- A 50 ml Schlenk flask was fitted with a condenser and a spin bar and flushed thoroughly with nitrogen. To the flask was added 2.0g (15 mmole) of AlCl_3 and 50 ml of anhydrous ether. 0.4g (10.5 mmole) of LiAlH_4 was cautiously added to the flask, followed by 0.5g (1.6 mmole) of 1'-benzylferrocene carbinol. The reaction was allowed to reflux for 1 hr. under nitrogen. After cooling, the reaction was worked up in the manner described above. The resulting product was chromatographed on silica gel eluted with hexane to yield 0.45g (1.55 mmole)

of 1-methyl-1'-benzylferrocene as a dark red oil. IR (#4): 3080(m), 3020(s), 3020(m), 2919(m), 1604(m), 1496(s), 1428(w), 1456(s), 1386(m), 1265(m), 1250(m), 1230(m), 1108(m), 1077(m), 1044(s), 1033(s), 1028(s). NMR (#4): (sigma values) 1.88(d, J=1Hz, .45), 1.94(s,3), 3.60(s, .45), 3.65(s, 1.5), 4.02(t, J=2.3Hz), 8.55, 7.21(s, 5.25). Mass Spec (Fig 4): 291.2 (22.2%), 290.2 (100%), 288.2(8.1%), 211.1(5.1%), 208.1(7.5).

1'-benzylferrocene carbinol chromium tricarbonyl (XXIX)- A 300 ml flask was fitted with a spin bar and condenser and thoroughly flushed with nitrogen. The flask was charged with 5.42g (17.7 mmole) of 1'-benzyl-ferrocene carbinol, 85 ml of dry dibutyl ether, 15 ml of dry THF, and 4.4g (20mmoles) of $\text{Cr}(\text{CO})_6$. The solution was allowed to reflux for 12 hrs. After cooling, the solution was filtered and the solvent removed by vacuum distillation. 50 ml of dry benzene was then added to the remaining oil and a tan precipitate formed. The precipitate was filtered to yield 0.7g (9% yield) of the chromium compound as a tan solid. MP: 200 C (decompose) IR (#5): 3430(s, broad), 2940(m), 1965(s), 1885(s, broad), 1550(s, broad), 1492(m), 1450(m), 1380(s), 1365(s), 1035(m).

1-methylenediphenylphosphite-1'-benzylferrocene chromium tricarbonyl (XXX)- A 100 ml flask was flushed thoroughly with nitrogen and fitted with a condenser. 0.7g (1.6 mmoles) of 1'-benzylferrocene carbonol chromium tricarbonyl, 35 ml of dry methylene chloride, .30 ml of chlorodiphenylphosphine (1.6 mmoles), and .50 ml (1.6 mmoles) of triethylamine were added to the flask. The solution was allowed to reflux for 4 days under a bleed of nitrogen. After refluxing, the solution had gone from clear colorless to chocolate brown. The solution was filtered under nitrogen to yield .45g of the starting chromium compound. The methylene chloride was removed from the filtrate in vacuo and the resulting brown oil was dissolved in 25 ml of dry benzene. The solution was filtered and the white solid discarded. The benzene was removed in vacuo and the remaining oil was dissolved in 10 ml of hot benzene and allowed to stand in the refrigerator overnight. The resulting solution and the white solid was discarded. Hexane was then added to the benzene filtrate until the cloud point was reached and the solution was quickly filtered to avoid decomposition. The resulting phosphite was isolated as .25g of a tan solid. ^{31}P NMR: (sigma value) +43.20 from phosphoric acid. IR: 3050(m), 2925(m), 1960(m), 1890(m), 1564(s), 1553(s), 1440(s), 1385(s), 1126(s), 1044(m), 1020(m), 995(m), 775(m), 720(s), 690(s).

Benzylferrocene (XXXI)- A 100 ml Schlenk flask was fitted with a spin bar and condenser and flushed thoroughly with nitrogen. The flask was charged with 2.0g (15 mmoles) of AlCl_3 and 50 ml of anhydrous ether. The system was allowed to stir for several minutes under nitrogen before addition of 0.5g (13.2 mmoles) of LiAlH_4 , being cautious to prevent too violent a reaction upon addition. 2.5g (8.6 mmoles) of benzoylferrocene was added to the flask, and the system was allowed to reflux under nitrogen for an

hour. After cooling, work up is the same as described for the other LiAlH_4 reductions. The ether layer is isolated and washed with 25 ml of H_2O , dried over MgSO_4 , and the solvent removed in vacuo. The resulting solid is recrystallized from pentane to yield the product as a yellow solid. 1.75g (73.42% yield) of the compound was recovered. MP: 72-76°C, Lit MP: 73-74°C⁴⁷ IR (#6): 3083(w), 3030(w), 2950(m), 1725(w), 1715(w), 16020(w), 1496(m), 1455(m), 1108(m), 1075(w), 1041(m), 1026(m). NMR (#5): (sigma values) 3.69(s, 2), 4.08(s, 5), 4.08(t, J=2.5Hz, 4), 7.23(s, 5.1).

Benzylferrocene chromium tricarbonyl⁴⁸ (XXXII)- A 250 ml flask was fitted with a spin bar and a condenser and flushed thoroughly with nitrogen. The flask was charged with 1.5g (5.4 mmoles) of benzylferrocene, 1.2g (5.5 mmoles) of chromium hexacarbonyl, 50 ml of dry, air-free benzene, and 14 ml of dry, air-free THF. The system was allowed to reflux for 4 days. After cooling, the solution was filtered and the solvent was removed by vacuum distillation. The remaining solid was extracted with hot hexane. The mustard yellow insoluble material yielded 1.23g (55.56% yield) of the chromium compound. MP: 148-49(decomp), 151-53(melt). Lit. MP⁴⁹: 164-65°C. IR (#7): 1973(s), 1890(s, broad), 1464(m), 1384(m), 1216(m), 1164(w), 1020(m), 1012(w), 994(m), 818(m), 660(s), 627(m), 496(m). The compound decomposed too quickly in either CDCl_3 or d_6 -benzene to obtain an NMR.

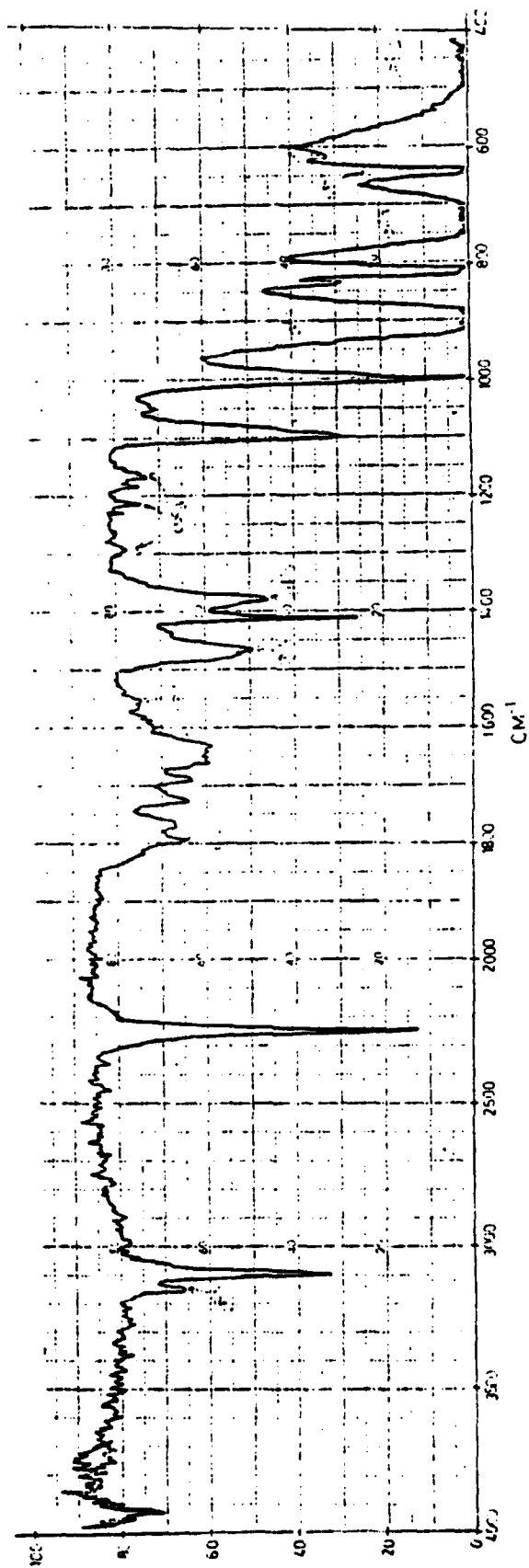
Benzylferrocene chromium dicarbonyl triphenylphosphine (XXXIII)- A photolysis apparatus was flushed thoroughly with nitrogen and charged with 0.8g (1.8 mmoles) of benzylferrocene chromium tricarbonyl, 0.5g (1.9 mmoles) of triphenylphosphine and 250 ml of dry, air-free benzene. The solution was photolyzed with a high intensity UV lamp for 24 hrs. under a bleed of nitrogen. The solution was then filtered and the benzene removed by vacuum distillation. The remaining orange oil was taken up in 50 ml of benzene and hexane was added to the cloud point. The solution was then filtered and the benzene removed from the filtrate in vacuo. The resulting orange oil was contaminated with triphenylphosphine. ^{31}P NMR shows a singlet (sigma value) 91.37 upfield of phosphoric acid.

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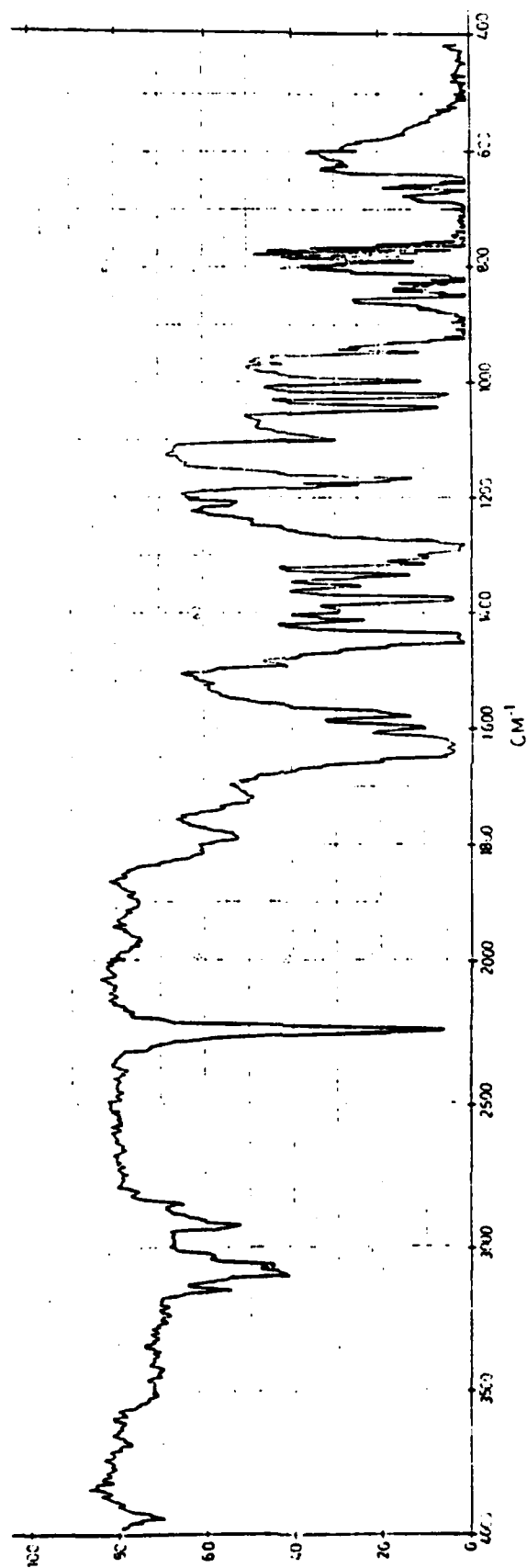
Appendix A

Infrared Spectra (IR)

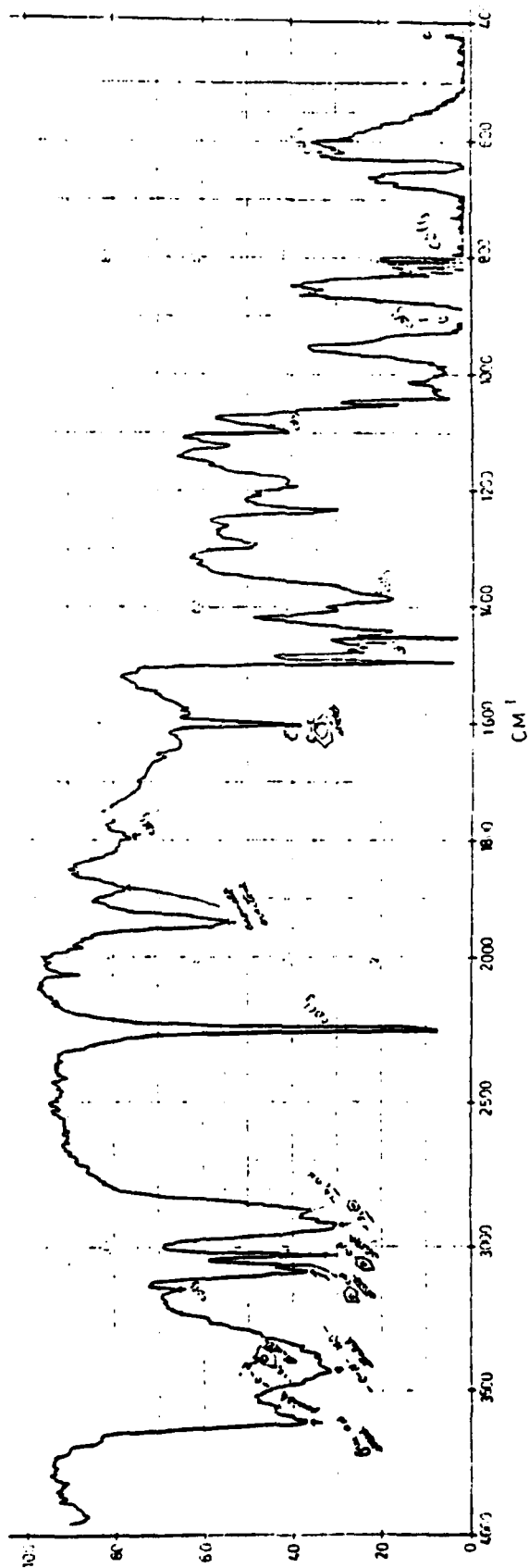
- 1) ferrocene
- 2) benzoylferrocene
- 3) 1'-benzylferrocenecarbinol
- 4) 1'methyl, 1'-benzylferrocene
- 5) 1'-benzylferrocenecarbinol chromium tricarbonyl
- 6) benzyl ferrocene
- 7) benzylferrocene chromium tricarbonyl



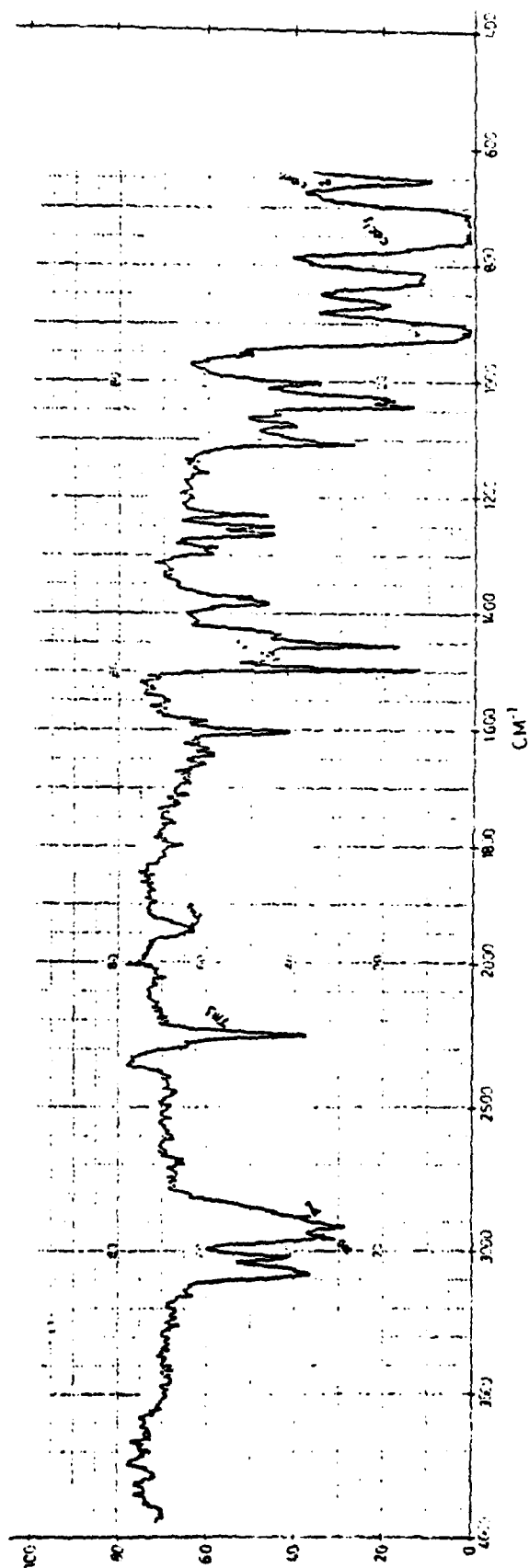
IR # 1

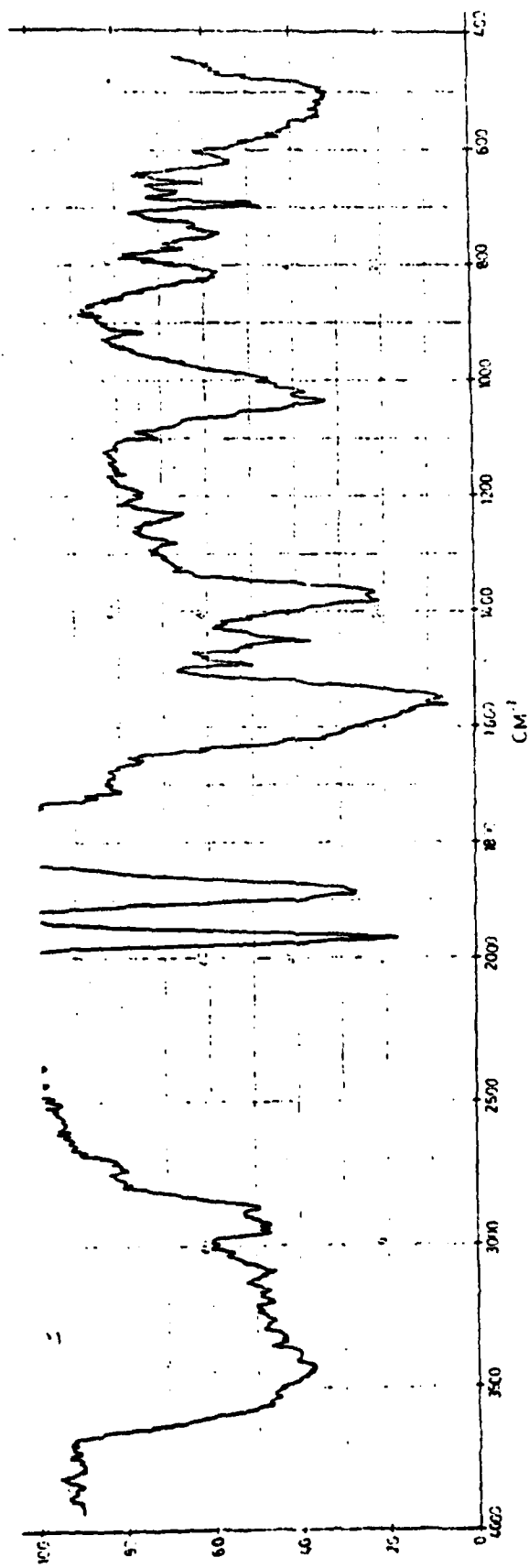


IR # 2

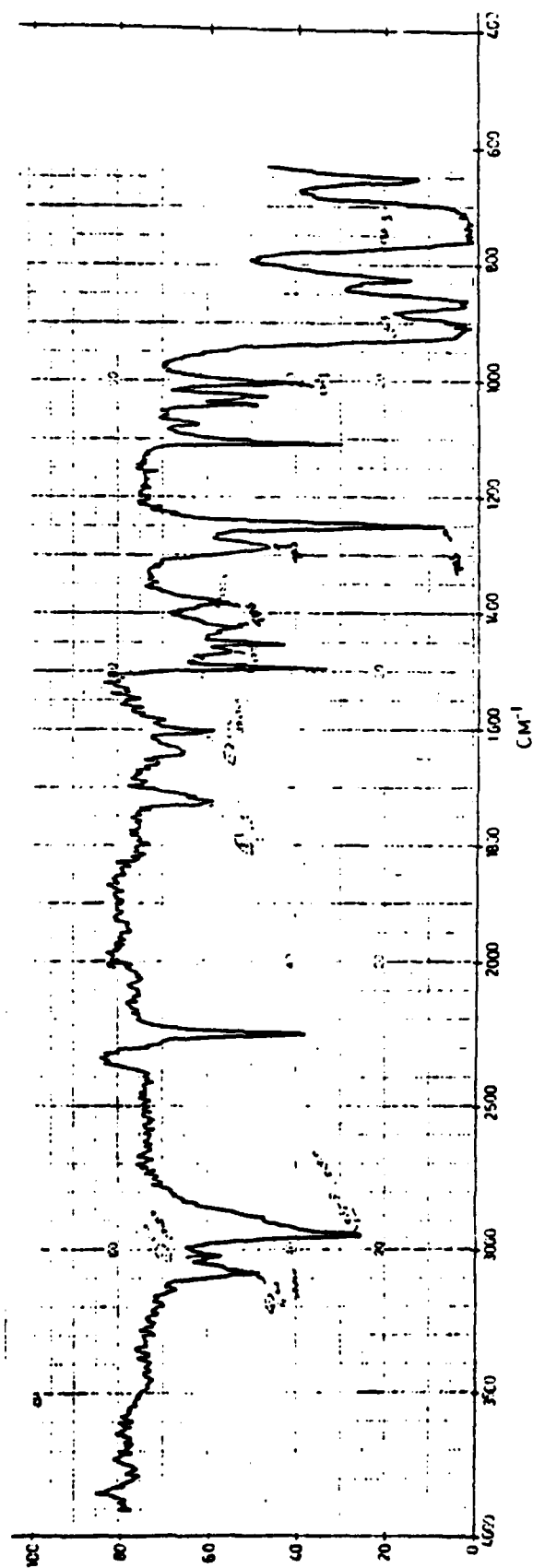


IR # 3

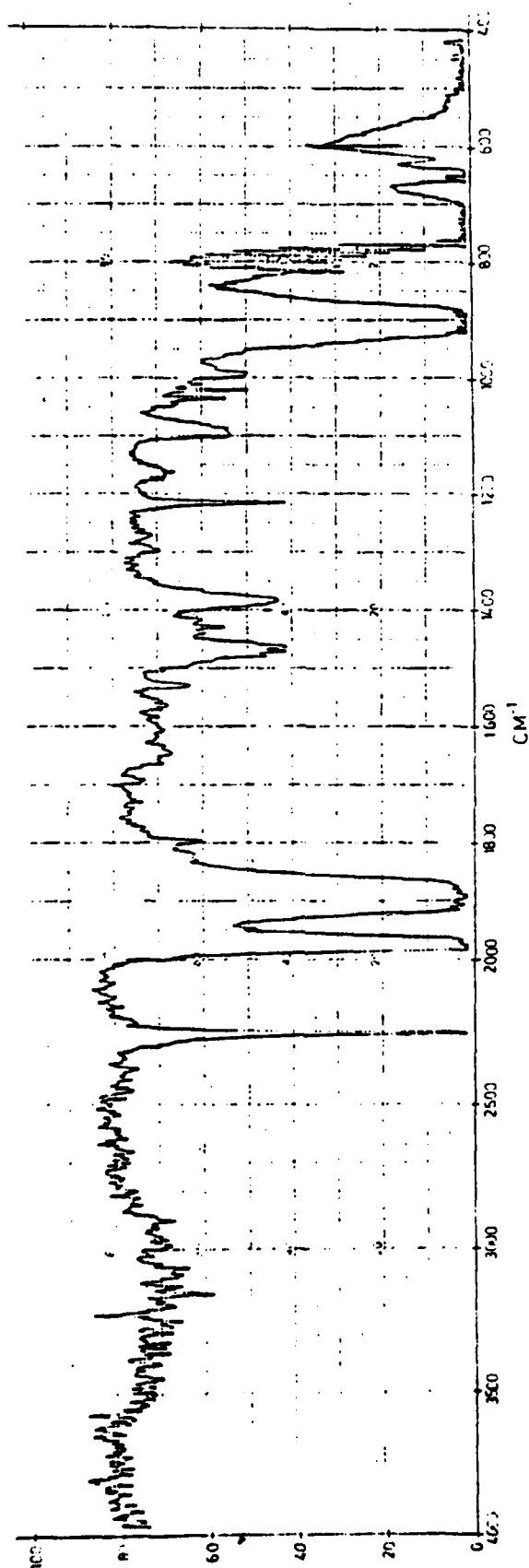




IR # 5



IR # 6

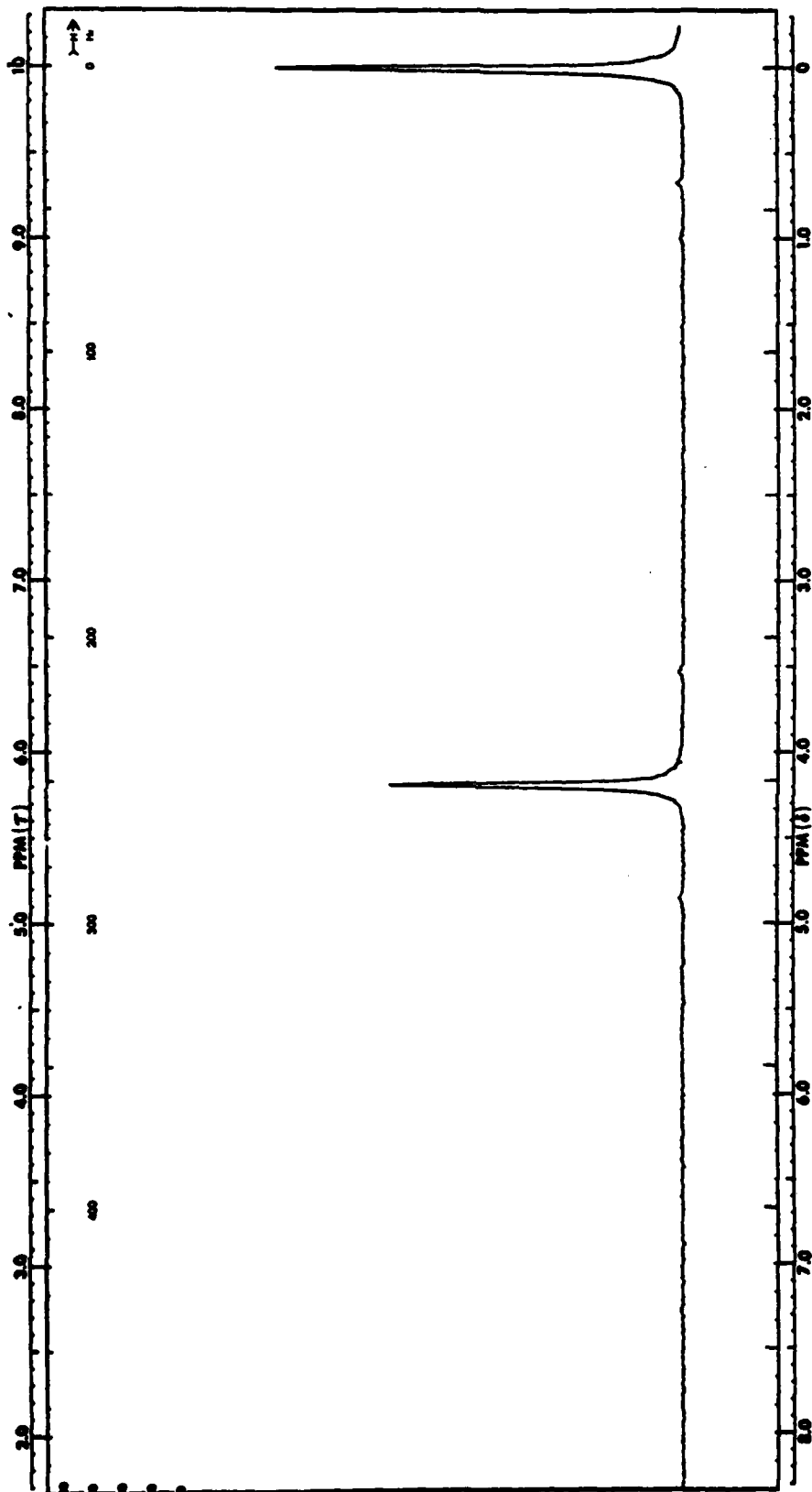


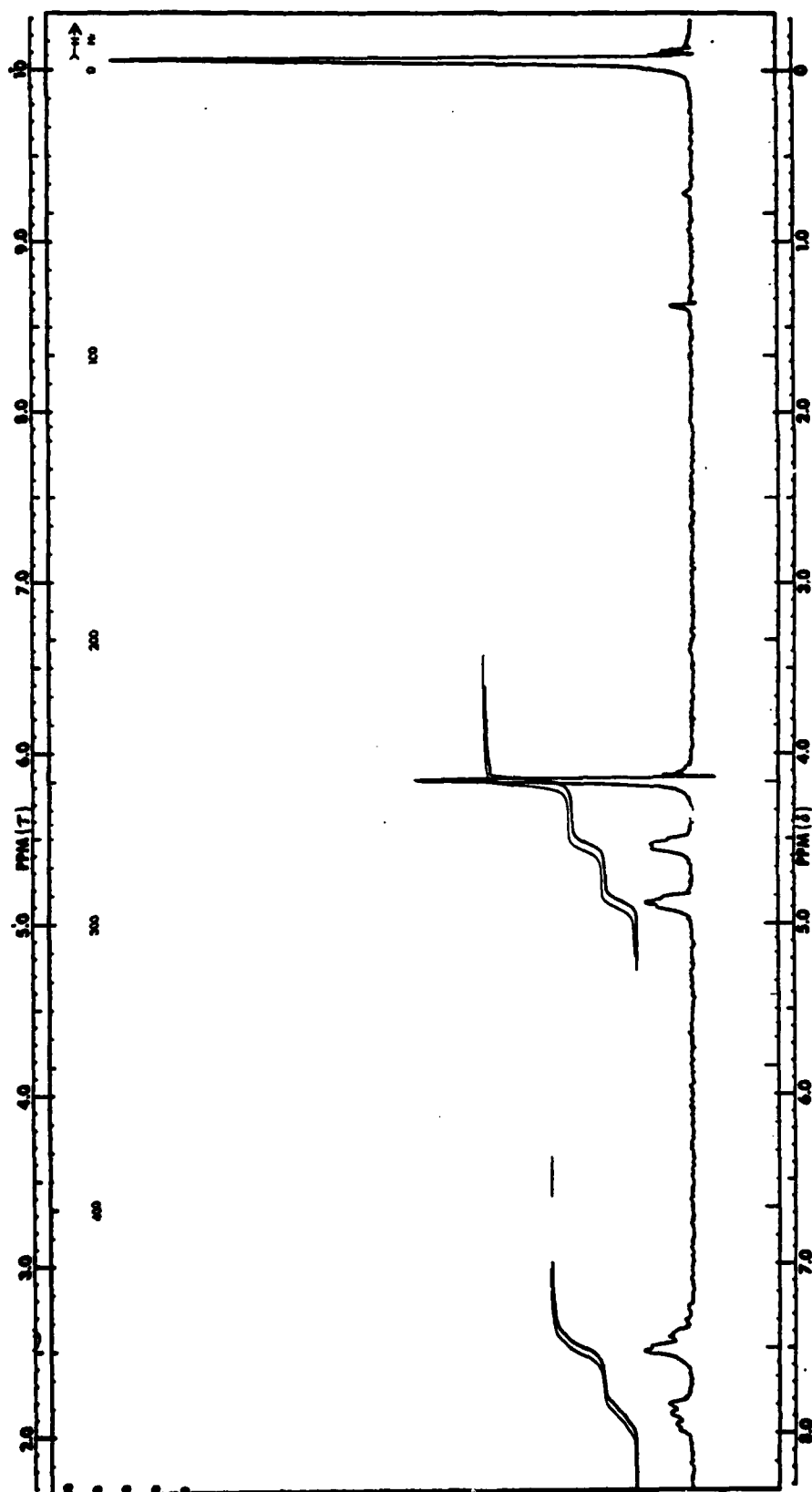
IR # 7

Appendix B

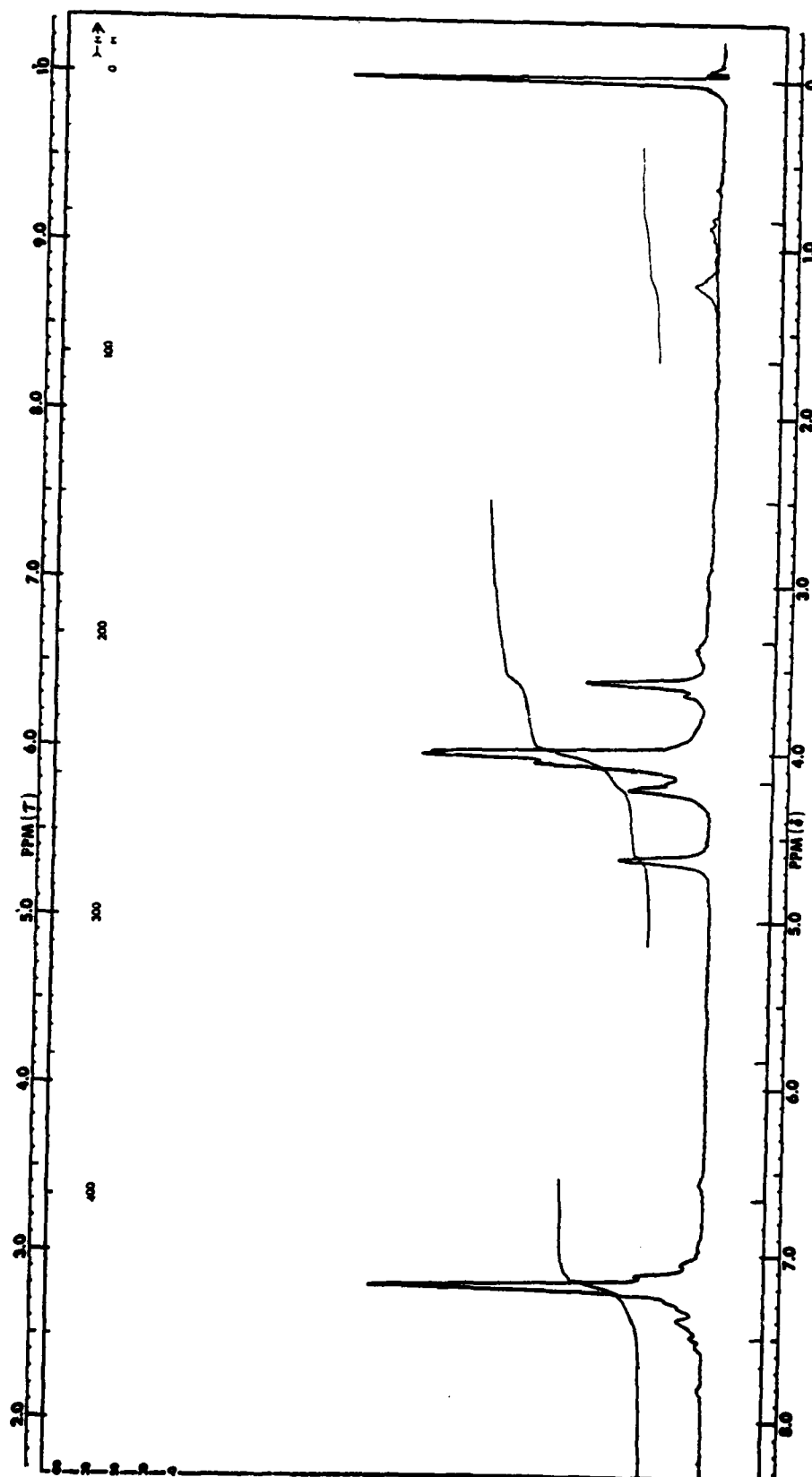
Nuclear Magnetic Resonance Spectra (NMR)

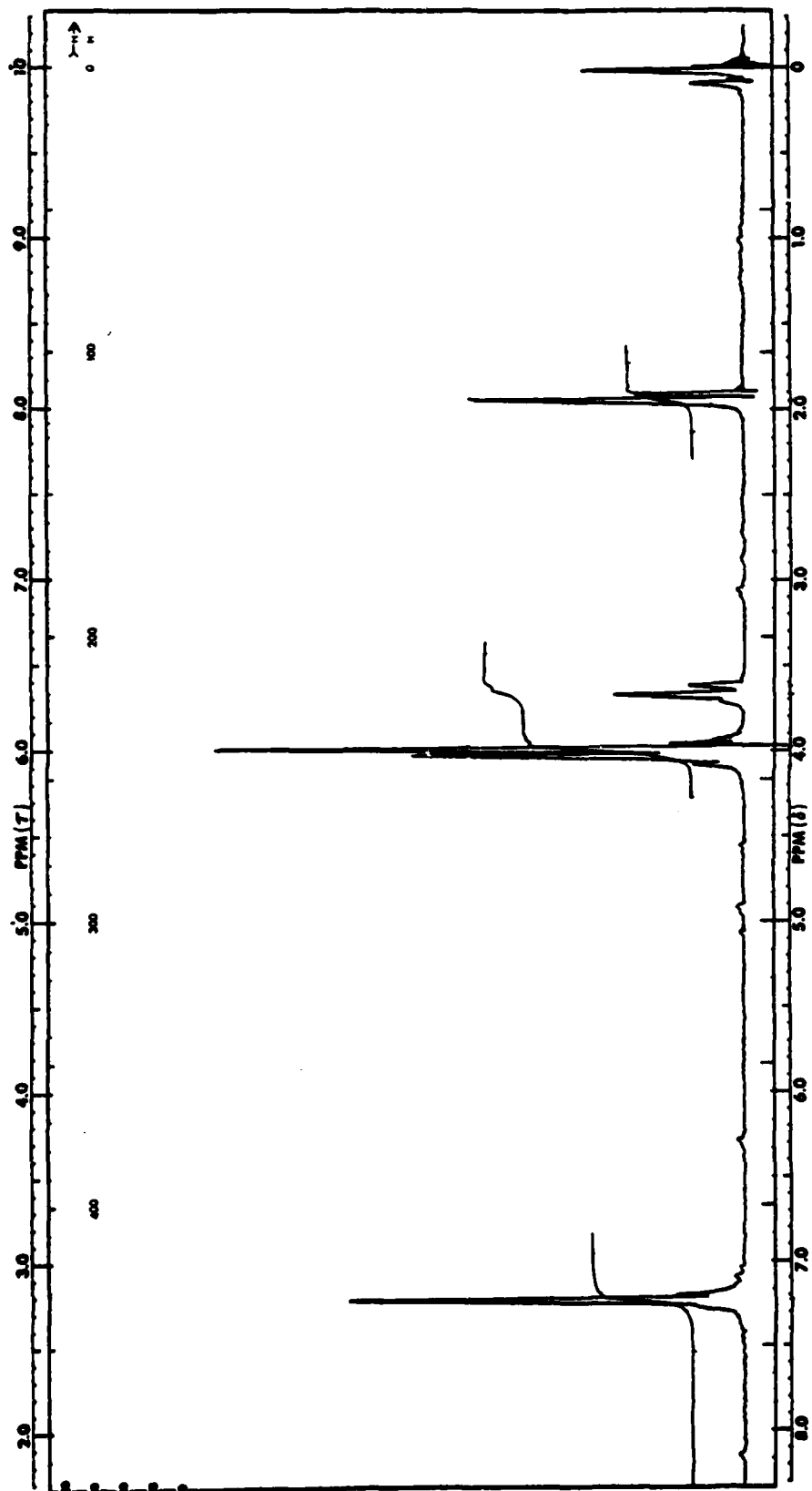
- 1) ferrocene
- 2) benzoylferrocene
- 3) 1'-benzylferrocenecarbinol
- 4) 1-methyl, 1'-benzylferrocene
- 5) benzylferrocene



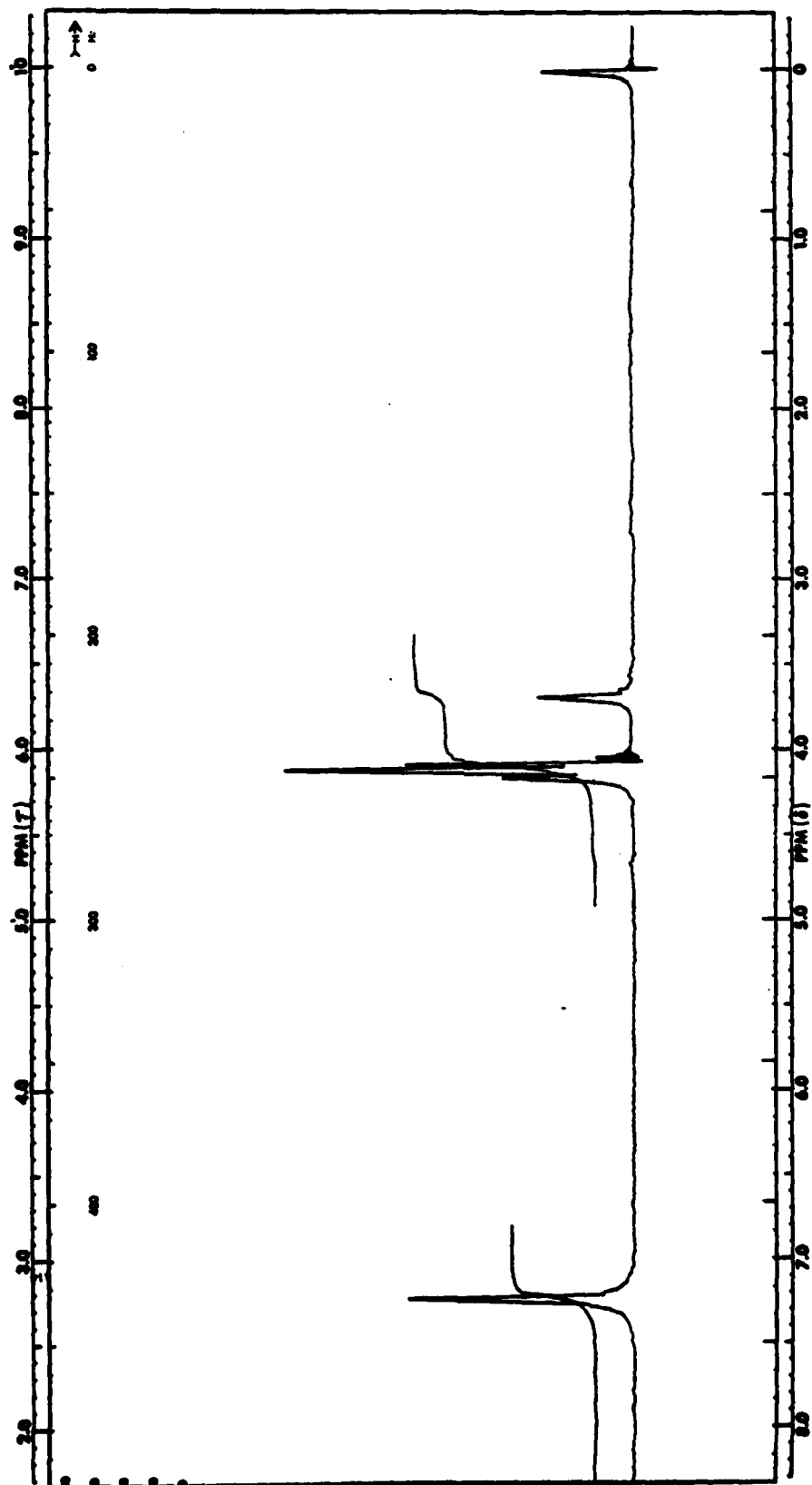


NMR # 2





NMR # 4



NMR # 5

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